THE PREPARATION OF CERTAIN COMPOUNDS CONTAINING THE PERFLUOROVINYL GROUP

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By

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A DISSERTATION PRESENTED TO THE GRADUATE COUNCIL OF
THE UNIVERSITY OF FLORIDA
IN PARTIAL FULFILMENT OF THE REQUIREMENTS FOR THE
DEGREE OF DOCTOR OF PHILOSOPHY

UNIVERSITY OF FLORIDA
January, 1955

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I INTRODUCTION

The crisis which was incurred by the shortage of natural rubber stock during the early stages of World War II served to emphasize the important role which rubber products had attained in our modern systems of transportation and communication. An intensified program of research and development achieved outstanding results in producing new types of synthetic rubber to meet the urgent needs of the armed forces and civilian population. While these new synthetics were in the most part satisfactory to alleviate the existing crisis, it was recognized by those of the rubber industry and armed services that a continued program of research and development in the field of rubber technology was necessary in order to meet the expanding requirements.

One of the principle concerns in recent years has been the relatively narrow temperature range in which present synthetic elastomers can be used satisfactorily. The rubber industry is using a variety of approaches to improve the materials currently in use; however, numerous workers in the field are of the opinion that the final answer must be in new elastomeric products. The use of fluorine compounds in the development of such elastomers has received considerable attention in recent studies on the problem.

The Office of the Quartermaster General is currently sponsoring a long-range Arctic Rubber Program for the purpose of discovering and developing rubber-like products which have the desired low-temperature properties, resistance to swelling when in contact with hydrocarbon fuels, and resistance to deterioration by oxidizing agents. The development of elastomers containing fluorine has been given a prominent part in this program due in part to the interesting and unique properties shown by the presently available fluoro-polymers, Teflon and Kel-F.

A number of approaches to the problem of synthesizing fluorine-containing elastomers was possible; however, it seemed desirable to utilize the knowledge and experience existing in the field of rubber technology as much as possible. Thus the classical approach was chosen: to introduce fluorine into the simple monomer molecules, to polymerize these and to compound the raw polymeric elastomer to give the desired rubber-like product. Since butadiene is used to a very great extent as a monomer in the currently existing synthetic rubbers, a logical step in this type of approach is the preparation of fluorobutadienes. The research described in this dissertation was undertaken as a part of the Arctic Rubber Program and describes the preparation of a number of fluorine-containing butadienes.

Until recently, little work had been done toward preparing fluorobutadienes. Mochel and Salisbury (21) had described the preparation of 2-fluorobutadiene using a method that involved the catalytic addition of anhydrous hydrogen fluoride to vinylacetylene according to the equation:

$$CH{\equiv}C\text{-}CH{=}CH_2 + HF \xrightarrow{HgO} CH_2{=}CFCH{=}CH_2.$$

This reaction, carried out in the gas phase, requires the use of special equipment and exact conditions of control of temperature, flow rates and catalyst preparation. It is further complicated by the explosive nature of vinylacetylene.

Wakefield (26) reported the synthesis of 2, 3-difluorobutadiene by the following approach:

$$CH_2{=}CH\text{-}CH{=}CH_2 + 2Cl_2 \longrightarrow CH_2ClCHClCHClCH_2Cl$$

$$CH_2ClCHClCHClCH_2Cl + 2KOH \longrightarrow CH_2{=}CCl\text{-}CCl{=}CH_2 + 2KCl + 2H_2O$$

$$CH_2{=}CCl\text{-}CCl{=}CH_2 + 2Cl_2 \longrightarrow CH_2ClCCl_2CCl_2CH_2Cl$$

$$CH_2ClCCl_2CCl_2CH_2Cl + 2HF \xrightarrow{HgO} CH_2ClCFClCFClCH_2Cl + 2HCl$$

$$CH_2ClCFClCFClCH_2Cl + 2Zn \longrightarrow CH_2{=}CF\text{-}CF{=}CH_2 + 2ZnCl_2$$

By a similar series of reactions (26) 2-fluoro-3-chlorobutadiene had been prepared. Both of these syntheses involve several steps including a fluorination step that gives low yields of the desired products.

The preparation of 1, 1-difluorobutadiene (25) and of 1, 1-difluoro-3-methylbutadiene (23) have recently been described in which the appropriate chloro compound was prepared, fluorinated, and dehalogenated to give the desired fluorobutadiene.

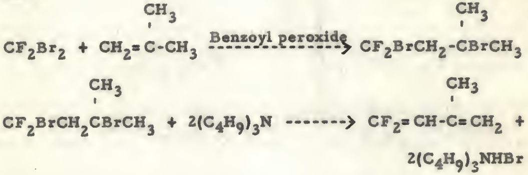
In all of the syntheses described above it was necessary to use a different series of reactions for each particular compound; no general method for preparing a particular type of fluorine-containing diene was set forth. Lovelace (17) working in this laboratory, recently described a method for the preparation of a number of 1, 1-difluorobutadienes. This method consists of adding dibromodifluoromethane or bromochlorodifluoromethane to olefins in the presence of an organic peroxide and eliminating two molecules of hydrogen halide from the resulting adduct. The preparation of 1, 1-difluorobutadiene as indicated by the following reactions is representative of this method.

$$CF_2Br_2 + CH_2{=}CHCH_3 \xrightarrow{\text{Benzoyl peroxide}} CF_2BrCH_2CHBrCH_3$$

$$CF_2BrCH_2CHBrCH_3 + 2(C_4H_9)_3N \longrightarrow CF_2{=}CH\text{-}CH{=}CH_2 + 2(C_4H_9)_3NHBr$$

By substituting other hydrocarbon olefins or fluoroölefins for propylene in the above reaction, a variety of 1, 1-difluorobutadienes was prepared. For example 1, 1, 2-trifluorobutadiene was prepared in this manner using 1-fluoropropylene and 1, 1, 3-trifluorobutadiene was prepared from 2-fluoropropylene. Similarly 1, 1-difluoromethylbutadienes were prepared from isobutylene and butene-2 as shown by the following sets of reactions:

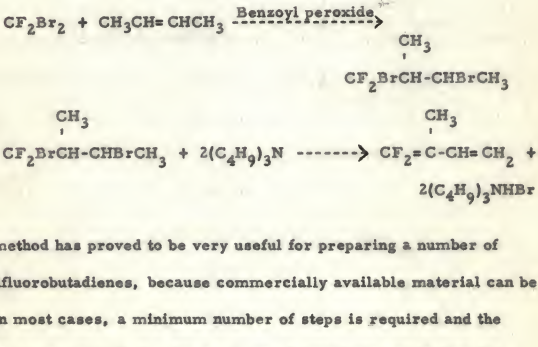
(1)



$$CF_2Br_2 + CH_2{=}\overset{CH_3}{C}{-}CH_3 \xrightarrow{\text{Benzoyl peroxide}} CF_2BrCH_2{-}\overset{CH_3}{C}BrCH_3$$

$$CF_2BrCH_2\overset{CH_3}{C}BrCH_3 + 2(C_4H_9)_3N \dashrightarrow CF_2{=}CH{-}\overset{CH_3}{C}{=}CH_2 + 2(C_4H_9)_3NHBr$$

(2)



$$CF_2Br_2 + CH_3CH{=}CHCH_3 \xrightarrow{\text{Benzoyl peroxide}} CF_2Br\overset{CH_3}{C}H{-}CHBrCH_3$$

$$CF_2Br\overset{CH_3}{C}H{-}CHBrCH_3 + 2(C_4H_9)_3N \dashrightarrow CF_2{=}\overset{CH_3}{C}{-}CH{=}CH_2 + 2(C_4H_9)_3NHBr$$

This method has proved to be very useful for preparing a number of 1, 1-difluorobutadienes, because commercially available material can be used in most cases, a minimum number of steps is required and the yields are generally high. However, few fluoroölefins other than the ethylenes are at present commercially available, so that the preparation of fluorobutadienes containing more than the two fluorine atoms in the number one position will involve the synthesis of the desired fluoroölefin. This in itself is often a laborious task and in many cases gives low yields of the desired olefin.

Very recently Tarrant and Gillman (24) have reported a method of preparing certain olefins and dienes which contain fluorine in the 1, 1, 2-positions. The method consists of reacting 2-chloro-1, 2-dibromo-1, 1, 2-trifluoroethane, which is readily prepared from the commercially available chlorotrifluoroethylene, with certain hydrocarbon olefins to give an addition product that can be converted to the appropriate 1, 1, 2-trifluoroölefin or diene. This procedure is outlined by the following reactions using propylene as an example.

$$CF_2{=}CFCl + Br_2 \xrightarrow{\qquad\qquad} CF_2BrCFClBr$$

$$CF_2BrCFClBr + CH_2{=}CHCH_3 \xrightarrow{\text{Benzoyl peroxide}} CF_2BrCFClCH_2CHBrCH_3$$

$$CF_2BrCFClCH_2CHBrCH_3 \xrightarrow{\text{Base}} CF_2BrCFClCH{=}CH\text{-}CH_3$$

$$CF_2BrCFClCH{=}CHCH_3 \xrightarrow{\text{Zn}} CF_2{=}CFCH{=}CHCH_3.$$

This procedure seemingly affords a general method of preparing substituted dienes containing the 1, 1, 2-trifluoro- group. However in all cases reported, only hydrocarbon olefins which are known to be reactive in this type of reaction were used. In no case was an attempt made to prepare dienes containing more than the three fluorine atoms.

Procedures are described in the following sections of this dissertation for the preparation of a number of fluorobutadienes containing, in addition to the perfluorovinyl group, one to three fluorine atoms on the carbon structure.

II DISCUSSION

In order to develop a method of preparing butadienes containing several fluorine atoms which would be suitable for large scale operations, careful consideration must be given to such factors as the availability of the starting materials, the convenience in carrying out the individual reactions leading to the final product and the yields obtained in these reactions. Thus a satisfactory synthesis would use readily available starting materials, could be carried out using convenient procedures and would give a high yield of the final product. Lovelace (17) showed that 1, 1-difluorobutadienes could be prepared in a minimum number of steps using commercially available materials by addition of halomethanes such as dibromodifluoromethane and bromochlorodifluoromethane to olefins to give adducts that were easily converted to the 1, 1-difluorobutadienes. It would seem that the addition of some commercially available haloethane containing fluorine atoms in the 1, 1, 2-positions to olefins would lead to a number of highly desirable butadienes containing an increased amount of fluorine.

At first thought it would appear that the readily available unsym-trichloro-trifluoroethane, Freon 113, would be a good starting point. It is conceivable that the addition of this material to ethylene would give 1, 1, 2-trifluorobutadiene in a three step process as shown below.

$$CF_2ClCFCl_2 + CH_2{=}CH_2 \xrightarrow{\text{Peroxide}} CF_2ClCFClCH_2CH_2Cl$$

$$CF_2ClCFClCH_2CH_2Cl \xrightarrow{\text{Base}} CF_2ClCFClCH{=}CH_2$$

$$CF_2ClCFClCH{=}CH_2 \xrightarrow{\text{Zn}} CF_2{=}CF\text{-}CH{=}CH_2$$

In addition, several fluorine-substituted ethylenes are at the present available that could be substituted for ethylene in the above process to give butadienes containing from three to six fluorine atoms per molecule. However, experimental work (2) showed unsym-trichlorotrifluoroethane to give only high boiling products in reactions of this type.

Kharasch (15) has shown, as a result of studies on tetrachloromethane and bromotrichloromethane that the substitution of a bromine atom for a chlorine results in an increased reactivity toward free radical attack. By analogy the compound 2-bromo-1, 2-dichloro-1, 1, 2-trifluoroethane should undergo free radical addition reactions more readily than trichlorotrifluoroethane. Unfortunately this compound is not readily available; however a similar compound 1, 2-dibromo-2-chloro-1, 1, 2-trifluoroethane can be obtained by reacting commercial chlorotrifluoroethylene with bromine,

$$CF_2{=}CFCl + Br_2 \longrightarrow CF_2BrCFClBr.$$

It was found that this compound reacted with ethylene in the presence of benzoyl peroxide to give a one-to-one addition product with the empirical formula $C_4H_4Br_2ClF_3$.

Kharasch (15) postulated the mechanism shown below to account for the formation of simple addition products from the peroxide induced reaction of polyhalomethanes with olefins of the type $CH_2{=}CHR$.

$$\text{I.}\quad CX_4 + (C_6H_5CO_2)_2 \dashrightarrow CX_3\cdot + C_6H_5X + C_6H_5CO_2\cdot + CO_2$$

$$\text{II.}\quad CX_3\cdot + CH_2{=}CHR \dashrightarrow CX_3CH_2\underset{\cdot}{C}HR$$

$$\text{III.}\quad CX_3CH_2\underset{\cdot}{C}HR + CX_4 \dashrightarrow CX_3CH_2CHXR + CX_3\cdot$$

$$\text{IV.}\quad CX_3CH_2\underset{\cdot}{C}HR + CH_2{=}CHR \dashrightarrow CX_3CH_2CH(R)CH_2\underset{\cdot}{C}HR$$

$$\text{V.}\quad CX_3CH_2CH(R)CH_2\underset{\cdot}{C}HR + CX_4 \dashrightarrow CX_3CH_2CH(R)CH_2CHXR + CX_3\cdot$$

There can be no doubt that this mechanism applies equally well in the case of the peroxide induced additions of 1,2-dibromo-2-chloro-1,1,2-trifluoroethane to olefins.

It is to be noted, however, that the homolytic scission of a carbon-bromine bond can conceivably occur at either end of the $CF_2BrCFClBr$ molecule to give one of the two radicals represented by A and B.

$CF_2BrCFCl\cdot$ A

$CFClBrCF_2\cdot$ B

Thus, for the addition of 1, 2-dibromo-2-chloro-1, 1, 2-trifluoroethane to ethylene, a symmetrical olefin, it would be possible to obtain either of the two compounds shown by C and D.

$CF_2BrCFClCH_2CH_2Br$ C

$CFClBrCF_2CH_2CH_2Br$ D

However, when the addition product is treated with alcoholic potassium hydroxide, the elimination of hydrogen bromide occurs to give an olefin which upon further reaction with zinc yields only the known (17) 1, 1, 2-trifluorobutadiene. This diene could be formed only from the compound represented above by C, thus indicating that the homolytic scission of the carbon-bromine bond must take place at the -CFClBr group rather than at the $-CF_2Br$ portion of the molecule. The general nature of the reaction of 1, 2-dibromo-2-chloro-1, 1, 2-trifluoroethane with hydrocarbon olefins has been further demonstrated by Gillman (3) using butene-1, butene-2, 2-methylpropene and octene-1. In all cases it was shown that the $CF_2BrCFCl\cdot$ radical was formed and that it attached itself to the methylene terminal of the double bond.

In order to obtain fluorobutadienes containing an increasing number of fluorine atoms per molecule, it seemed advisable to investigate the reactions of 1,2-dibromo-2-chloro-1,1,2-trifluoroethane with fluoroölefins. Haszeldine (8) and Lovelace (17) have shown that for a number of fluoroölefins addition of a trihalomethyl radical takes place at the carbon atom containing the least number of fluorine atoms. Thus, trifluoromethyl iodide was reacted with fluoroethylene to give 3-iodo-1,1,1,3-tetrafluoropropane, and dibromodifluoromethane was shown to yield 1,3-dibromo-1,1,3-trifluoropropane when reacted with the same olefin. Simiiarly 1,2-dibromo-2-chloro-1,1,2-trifluoroethane has been shown to follow a like course to give 1,4-dibromo-2-chloro-1,1,2,4-tetrafluorobutane by reaction with fluoroethylene. 1,1-Difluoroethylene gave the adduct $CF_2BrCFClCH_2CF_2Br$ from which hydrogen bromide was easily eliminated by treatment with a base. Trifluoroethylene reacted with 1,2-dibromo-2-chloro-1,1,2-trifluoroethane to give the one-to-one adduct $CF_2BrCFClCHFCF_2Br$ which is converted to perfluorobutadiene by the elimination of hydrogen bromide upon treatment with a base followed by the removal of bromine and chlorine atom with zinc. The one-to-one addition products of 1,2-dibromo-2-chloro-1,1,2-trifluoroethane and the above fluoroethylenes are described in Table I.

It is interesting to note from a comparison of the results obtained from the reaction of 1,2-dibromo-2-chloro-1,1,2-trifluoroethane with the ethylene series of olefins, that an increase in the fluorine substitution on the ethylene exerts a pronounced effect on the yield of the resulting addition products. For example, ethylene yielded only the one-to-one adduct; fluoroethylene, while yielding predominately the one-to-one addition product also gave a small amount of the two-to-one adduct; 1,1-difluoroethylene showed a decrease in the amount of one-to-one adduct with a considerable increase in the two-to-one adduct, and trifluoroethylene produced only 16% of the one-to-one adduct, a larger amount of the two-to-one product and a considerable amount of high-boiling residue. Reaction with 1-chloro-1-fluoroethylene and chlorotrifluoroethylene failed to give a simple addition product under the conditions of the experiment.

It is thus evident that the replacement of hydrogen by fluorine in the olefin molecule exerts a pronounced retarding effect toward the simple addition reaction. The two competing reactions of the intermediate free radical, $CF_2BrCFClCHXCX_2\cdot$ where X may be either a hydrogen or fluorine atom, are represented by VI and VII.

$$\text{VI.}\quad CF_2BrCFClCHXCX_2\cdot + CF_2BrCFClBr \longrightarrow CF_2BrCFClCHXCX_2Br + CF_2BrCFCl\cdot$$

$$\text{VII.}\quad CF_2BrCFClCHXCX_2\cdot + CHX{=}CX_2 \longrightarrow CF_2BrCFClCHXCX_2CHXCX_2\cdot$$

The apparent effect of fluorine substitution on the olefin is to render the

TABLE I

THE PROPERTIES OF THE ADDITION PRODUCTS OF FLUOROÖLEFINS AND 1,2-DIBROMO-2-CHLORO-1,1,2-TRIFLUOROETHANE

Olefin	Addition Product	Yield	B. P.		t	n_D^t	d_4^t	MR_D		Silver Equiv.	
		%	°C	mm.	°C			Calc.	Found	Calc.	Found
$CH_2=CH_2$	$CF_2BrCFClCH_2CH_2Br$	58	67.4	20	25	1.4563	2.035	41.08	40.67	101.5	101.9
$CH_2=CHF$	$CF_2BrCFClCH_2CHFBr$	74	72	32	25	1.4405	2.075	41.08	41.00	107.4	106.5
	$CF_2BrCFClCH_2CHFCH_2CHFBr$	6.4	104.5	15	27	1.4428	1.946	50.30	50.13	122.8	122.7
$CH_2=CF_2$	$CF_2BrCFClCH_2CF_2Br$	44	70.1	50	27	1.4230	2.063	41.08	41.03	113.4	111.9
	$CF_2BrCFClCH_2CF_2CH_2CF_2Br$	23.4	90-91	20	27	1.4112	2.014	49.61	50.30	134.7	133.6
$CHF=CF_2$	$CF_2BrCFClCHFCF_2Br$	16.2	61.5	40	23	1.4330	2.013	41.07	46.27	116.1	116.4
	$CF_2BrCFClCHFCF_2CHFCF_2Br$	20	79.5	15	25	1.3943	2.077	50.31	50.75	146.8	147.0

intermediate radical $CF_2BrCFClCHXCX_2\cdot$ insufficiently reactive to bring about the homolytic scission of the carbon-bromine bond of a $CF_2BrCFClBr$ molecule to complete the formation of a one-to-one addition product as in VI above. It must therefore accept an alternate route of reacting with a second olefin molecule leading to the formation of two-to-one and higher adducts. With hydrocarbon olefins reaction VI predominates to the extent that no higher adducts than the one-to-one products were formed.

In all cases of the additions of 1,2-dibromo-2-chloro-1,1,2-trifluoroethane to fluoroethylenes, the two-to-one adduct was found to accompany the formation of the one-to-one addition product. The steps representing the addition of 1,2-dibromo-2-chloro-1,1,2-trifluoroethane to fluoroethylene are shown below.

VIII. $CF_2BrCFClBr + (C_6H_5CO_2)_2 \dashrightarrow CF_2BrCFCl\cdot +$
$C_6H_5Br + C_6H_5CO_2\cdot + CO_2$

IX. $CF_2BrCFCl\cdot + CH_2{=}CHF \dashrightarrow CF_2BrCFClCH_2\underset{\cdot}{C}HF$

X. $CF_2BrCFClCH_2\underset{\cdot}{C}HF + CF_2BrCFClBr \dashrightarrow$
$CF_2BrCFClCH_2CHFBr + CF_2BrCFCl\cdot$

XI. $CF_2BrCFClCH_2\underset{\cdot}{C}HF + CH_2{=}CHF \dashrightarrow$
$CF_2BrCFClCH_2CHFCH_2\underset{\cdot}{C}HF$

XII. $CF_2BrCFClCH_2CHFCH_2\underset{\cdot}{C}HF + CF_2BrCFClBr \dashrightarrow$
$CF_2BrCFClCH_2CHFCH_2CHFBr + CF_2BrCFCl\cdot$

The formation of the one-to-one adduct is indicated in step X while the two-to-one is formed by reaction XII. It was shown earlier that the 1-bromo-2-chloro-1,1,2-trifluoroethyl radical attaches itself to the carbon containing the least number of fluorine atoms to form the intermediate radical as in step IX; there is no evidence to show that this intermediate radical does not react with a second olefin molecule in the same manner, indicated by step XI, to form the higher adduct. The two-to-one addition product from 1,1-difluoroethylene was assigned the structure $CF_2BrCFClCH_2CF_2CH_2CF_2Br$ on this basis, while the two-to-one adduct from trifluoroethylene was assigned the structure $CF_2BrCFClCHFCF_2CHFCF_2Br$. The properties of these adducts are further described in Table I.

The reaction of 1,2-dibromo-2-chloro-1,1,2-trifluoroethane with 1,1-difluoropropene-1 and with 1-chloro-1-fluoroethylene failed to give any addition product and the olefins were recovered unreacted. Since it is known that the decomposition of the peroxide results in the formation of the radical $CF_2BrCFCl\cdot$ as in reaction VIII above, there is no reason to believe that this radical does not then react with an olefin molecule to give the intermediate radical $CF_2BrCFClCH(CH_3)\dot{C}F_2$, in the case of 1,1-difluoropropene-1, according to step IX. In view of the absence of an addition product and the recovery of unreacted olefin, one is led to believe that the intermediate radical

$CF_2BrCFClCH(CH_3)CF_2\cdot$ is not sufficiently reactive to abstract a bromine atom from another $CF_2BrCFClBr$ molecule and thus fails to perpetuate the reaction. The intermediate radical thus formed may terminate the reaction by several possible methods. It may lose a hydrogen atom to give an olefin, $CF_2BrCFClC(CH_3){=}CF_2$, or it may combine with another free radical. Since benzoic acid has been isolated from reactions of this type when benzoyl peroxide is used as a catalyst, it is quite probable that loss of hydrogen occurs to some extent.

In view of the lack of reactivity of 1, 2-dibromo-2-chloro-1, 1, 2-trifluoroethane toward a number of fluoroölefins to give the desired one-to-one addition products, a search was made to find a more reactive material containing the 1, 1, 2-trifluoro configuration. Haszeldine (7) prepared 1, 2-dichloro-2-iodo-1, 1, 2-trifluoroethane in good yields by the addition of iodine monochloride to chlorotrifluoroethylene and showed it to be very reactive toward free radical attack. As an example he was able to bring about the formation of 1, 2, 3, 4-tetrachlorohexafluorobutane by irradiation of 1, 2-dichloro-2-iodo-1, 1, 2-trifluoroethane with ultraviolet light in the presence of mercury according to the equation:

$$2\ CF_2ClCFClI + Hg \dashrightarrow CF_2ClCFClCFClCF_2Cl + HgI_2$$

The 1, 2, 3, 4-tetrachlorohexafluorobutane was then converted to perfluorobutadiene by reaction with zinc, thus establishing the transitory existence of the $CF_2ClCFCl\cdot$ radical.

The pronounced reactivity of 1, 2-dichloro-2-iodo-1, 1, 2-trifluoroethane is further demonstrated in the present research by the high yields of one-to-one addition products obtained by reacting it with a number of fluoroölefins that failed to give satisfactory yields of addition products with 1, 2-dibromo-1-chloro-1, 1, 2-trifluoroethane. For instance reaction with trifluoroethylene gave a 79% conversion to the one-to-one adduct and none of the two-to-one product, 1, 1-difluoropropene gave only the one-to-one addition product in an 89% conversion and 1-chloro-1-fluoroethylene produced a 45% conversion to the one-to-one adduct. The products derived from the additions of 1, 2-dichloro-2-iodo-1, 1, 2-trifluoroethane to 1-chloro-1-fluoroethylene, chlorotrifluoroethylene, trifluoroethylene, 1, 1-difluoropropene-1, 3, 3, 3-trifluoropropene-1 and 2-trifluoromethylpropene are further described in Table II.

The mode of addition of 1, 2-dichloro-2-iodo-1, 1, 2-trifluoroethane to fluoroölefins was found to be the same as that described for the reactions of 1, 2-dibromo-2-chloro-1, 1, 2-trifluoroethane. The structure of the adduct of trifluoroethylene was established as $CF_2ClCFClCHFCF_2I$ by its conversion to perfluorobutadiene when treated with a base, which removed hydrogen iodide, followed by reaction with zinc to eliminate chlorine. The adduct of 1-chloro-1-fluoroethylene

TABLE II

THE PROPERTIES OF THE ADDITION PRODUCTS OF FLUOROÖLEFINS AND 1,2-DICHLORO-2-IODO-1,1,2-TRIFLUOROETHANE

Olefin	Addition Product	Yield %	B.P. °C	B.P. mm.	t °C	n_D^t	d_4^t	MR_D Calc.	MR_D Found	Silver Equiv. Calc.	Silver Equiv. Found
$CH_2{=}CFCl$	$CF_2ClCFClCH_2CFClI$	45	70	10	22	1.4741	2.075	48.07	48.68	89.8	90.0
$CHF{=}CF_2$	$CF_2ClCFClCHFCF_2I$	79	56	23	28	1.4224	2.110	43.21	43.49	120.3	120.0
$CF_2{=}CFCl$	$CF_2ClCFClCF_2CFClI^a$	26	74.0	24	22	1.4405	2.182	48.21	47.8		
$CH_2{=}CHCF_3$	$CF_2ClCFClCH_2\overset{CF_3}{\overset{\vert}{C}}HI$	95	61	18	22	1.4275	2.013	47.82	47.91	124.97	125.9
$CF_2{=}CHCH_3$	$CF_2ClCFCl\overset{CH_3}{\overset{\vert}{C}}HCF_2I$	89	75.5	20	25	1.4567	1.994	47.82	48.72	119.0	119.2
$CH_2{=}\underset{CF_3}{\underset{\vert}{C}}CH_3$	$CF_2ClCFClCH_2\overset{CF_3}{\overset{\vert}{C}}ICH_3$	87	65.5	12	22	1.4418	1.947	52.45	52.84	129.64	129.2

a. Previously reported by Miller (see reference 20) was assigned the structure $CF_2ClCFClCH_2CFClI$, because of its conversion to 4-chloro-1, 1, 2, 4-tetrafluorobutadiene when treated in the same manner. Miller (20) has previously carried out the addition of 1, 2-dichloro-2-iodo-1, 1, 2-trifluoroethane to chlorotrifluoroethylene and showed the one-to-one adduct obtained to have the structure $CF_2ClCFClCF_2CFClI$ on the basis of its conversion to $CF_2=CFCF_2CHClF$ and not to $CF_2=CF-CF=CF_2$ by zinc in ethanol. The addition reaction was repeated in the present research and similar results were obtained.

The one-to-one addition product obtained from 1, 1-difluoropropene-1 was found to have the structure $CF_2ClCFClCH(CH_3)CF_2I$ since reaction with base brought about elimination of hydrogen iodide and further treatment with zinc gave the conjugated diene, 2-methyl-1, 1, 3, 4, 4-pentafluorobutadiene. Similarly the one-to-one adduct from 3, 3, 3-trifluoropropene-1 and 1, 2-dichloro-2-iodo-1, 1, 2-trifluoroethane was assigned the structure $CF_2ClCFClCH_2CHICF_3$, since it was shown above that 1, 2-dichloro-2-iodo-1, 1, 2-trifluoroethane follows the same pattern in addition reactions as does the halomethanes and Haszeldine (6) has shown that trifluoromethyl iodide reacts with 3, 3, 3-trifluoropropene-1 to give 2-iodo-1, 1, 1, 4, 4, 4-hexafluorobutane.

It is interesting to note that, although dibromodifluoromethane failed to react with 2-trifluoromethylpropene (17), 1,2-dichloro-2-iodo-1,1,2-trifluoroethane reacted with this olefin giving an 85% conversion to the one-to-one adduct. The structure of this product was shown to be $CF_2ClCFClCH_2C(CF_3)ICH_3$ due to its conversion to 1,1,2-trifluoro-4-trifluoromethylpentadiene-1,3 by a two step reaction with a strong base and with zinc.

It should be noted that no adduct higher than the one-to-one product was isolated from any of the reactions involving 1,2-dichloro-2-iodo-1,1,2-trifluoroethane and fluoroölefins. This is a noticeable contrast to the comparable reactions of 1,2-dibromo-2-chloro-1,1,2-trifluoroethane in which large quantities of two-to-one adducts were obtained. It is not surprising however, in view of the greater reactivity of the carbon-iodine bond toward radical attack as compared to the carbon-bromine bond. The controlling reaction, as with the 1,2-dibromo-2-chloro-1,1,2-trifluoroethane reactions, is the course taken by the intermediate radical as indicated by equations XIII and XIV for the addition to a fluoroölefin of the type $CHX{=}CX_2$ where X may be hydrogen, fluorine or an alkyl group.

XIII. $CF_2ClCFClCHX\underset{\cdot}{C}X_2 + CF_2ClCFClI \dashrightarrow CF_2ClCFClCHXCX_2I + CF_2Cl\underset{\cdot}{C}FCl$

XIV. $CF_2ClCFClCHX\underset{\cdot}{C}X_2 + CHX{=}CX_2 \dashrightarrow CF_2ClCFClCHXCX_2CHXCX_2\cdot$

Thus with 1, 2-dichloro-2-iodo-1, 1, 2-trifluoroethane the carbon-iodine bond is sufficiently reactive to cause reaction XIII to take place so rapidly that reaction XIV does not occur.

Although 1, 2-dichloro-2-iodo-1, 1, 2-trifluoroethane undergoes free radical addition to fluoroölefins to produce one-to-one adducts with greater facility than does 1, 2-dibromo-2-chloro-1, 1, 2-trifluoroethane, it failed to produce addition products with the highly halogenated olefins, 2-H-pentafluoropropylene and perfluoropropylene. The reason for the lack of reactivity with these olefins is not completely understood. In both cases the olefins were recovered in almost quantitative amounts. These olefins also fail to undergo free radical addition reactions with other halogenated compounds such as dibromodifluoromethane (17) and 1, 2-dibromo-2-chloro-1, 1, 2-trifluoroethane; however, under extreme conditions they have been made to react with trifluoromethyl iodide (9).

The value of the one-to-one adducts obtained from the reactions of 1, 2-dibromo-2-chloro-1, 1, 2-trifluoroethane and 1, 2-dichloro-2-iodo-1, 1, 2-trifluoroethane with olefins lies in their ready conversion to dienes containing the perfluorovinyl group. The adducts were converted into olefins by reaction with bases and into dienes by reaction of the olefins with zinc. These reactions are represented below, for the formation of 1, 1, 2-trifluorobutadiene, by equations XV and XVI.

$$\text{XV.}\quad CF_2BrCFClCH_2CH_2Br \xrightarrow{\text{Base}} CF_2BrCFClCH{=}CH_2$$

$$\text{XVI.}\quad CF_2BrCFClCH{=}CH_2 \xrightarrow{\text{Zn}} CF_2{=}CF\text{-}CH{=}CH_2$$

Using this procedure the following conjugated dienes were prepared: 1, 1, 2-trifluorobutadiene, 1, 1, 2, 4-tetrafluorobutadiene, 2-H-pentafluorobutadiene, perfluorobutadiene, 1-chloro-1, 3, 4, 4-tetrafluorobutadiene, 2-methyl-1, 1, 3, 4, 4-pentafluorobutadiene, 3, 4-di H-hexafluoropentadiene-1, 3 and 1, 1, 2-trifluoro-4-trifluoromethylpentadiene-1, 3. The structures and physical properties of these dienes are further described in Table IV.

The dehydrohalogenation of the adducts, equation XV, took place readily by refluxing with aqueous potassium hydroxide solutions in all cases except for 1, 4-dibromo-2-chloro-1, 1, 2-trifluorobutane which required alcoholic potassium hydroxide. It is to be expected that this adduct should require the stronger base in view of the absence of the strongly electronegative fluorine atoms on either of the carbon atoms from which the hydrohalide was removed. The yields of olefins were generally high for reactions of this type. This can be attributed to the lack of ether formation which usually takes place when alcoholic alkali is used, but does not occur in aqueous solutions. It is interesting to note that in every case hydrogen bromide or hydrogen iodide was removed in preference to hydrogen chloride. It is thus evident that the bromine and iodine atoms are not so strongly held by the carbon as is the chlorine, which is held closer to a carbon atom because of the electron draining property of the fluorine atoms. The fluoroölefins produced from the addition products and their physical constants are shown in Table III.

The dehalogenation of the intermediate olefins gave good yields of the corresponding fluorine substituted dienes. The reaction with zinc as shown by equation XVI was carried out using an alcohol solvent. The choice of alcohol was determined by the particular diene produced. Since it was desirable in carrying out the reactions to distill the resulting diene from the reaction mixture as it was formed, thereby minimizing the possibility of polymerization of the diene, an alcohol that had a boiling point considerably above that estimated for the diene to be formed was chosen. The structures and physical properties of the dienes prepared are given in Table IV.

When the dehydrohalogenation and dehalogenation steps were carried out in the reverse order, considerably lower yields of products resulted. Thus when 1, 4-dibromo-2-chloro-1, 1, 2-trifluorobutane was treated with a mixture of zinc and propanol-2 in the customary manner only 29% of the expected 4-bromo-1, 1, 2-trifluorobutene-1 was formed. However, an appreciable quantity of 1, 1, 2-trifluorobutene-1 was also produced as a result of the replacement of the bromine atom on the terminal methylene group of 4-bromo-1, 1, 2-trifluorobutene-1 by hydrogen. When the reaction was carried out using zinc dust and 1.5 N

TABLE III

THE PROPERTIES OF OLEFINS OBTAINED FROM THE ADDITION PRODUCTS

Compound	B. P. °C	t °C	n_D^t	d_4^t	MR_D[a] calc.	MR_D[a] found	Analysis calc.	Analysis found
$CH_2{=}CHCFClCF_2Br$	99.5	25	1.4092	1.678	32.84	32.93	111.7	113.4[b]
$CHF{=}CHCFClCF_2Br$	97-97.3	25	1.3961	1.781	32.44	32.58	120.7	121.3[b]
$CF_2{=}CHCFClCF_2Br$	91.0	24	1.3837	1.838	32.84	32.97	129.7	130.2[b]
$CF_2{=}CFCFClCF_2Cl$[a]	65.5-67	22	1.3440	1.615	29.9	30.5		
$CF_2{=}\overset{CH_3}{C}CFClCF_2Cl$	100.5	22	1.3746	1.515	34.56	34.64	31.3	31.4[c]
$CH_3\text{-}\overset{CF_3}{C}{=}CHCFClCF_2Cl$	109.5	20	1.3675	1.485	39.18	39.51	27.20	26.9[c]
$CF_3CH{=}CHCFClCF_2Cl$	87.5	23	1.3472	1.519	34.56	34.78	28.75	29.0[c]
$CF_2{=}CFCH_2CH_3$	14.2							
$CF_2{=}CFCH_2CH_2Br$	95	22	1.4022	1.660	28.0	29.1	42.24	42.4[d]
$CF_2ClCFClCH{=}CFCl$	102.5	24	1.3993	1.586	34.81	35.28	45.96	45.7[c]

a. Previously reported by Miller (See reference 19)
b. Silver equivalent
c. % chlorine
d. % bromine

TABLE IV

THE PROPERTIES OF DIENES OBTAINED FROM THE ADDITION PRODUCTS

Compound	B. P. °C	t °C	n_D^t	d_4^t	MR_D Calc.	MR_D Found	Analysis Calc.	Analysis Found
$CF_2{=}CF{-}CH{=}CH_2$	7.8-8.0						108.1	109.5[b]
$CF_2{=}CF{-}CH{=}CHF$	16.5	0	1.3427	1.342	19.74	19.84	126.1	122.8[b]
$CF_2{=}CF{-}CH{=}CF_2$	15.5						144.1	145.2[b]
$CF_2{=}CF{-}CF{=}CF_2$[a]	7.1-7.3							
$CF_2{=}CF{-}\overset{CH_3}{C}{=}CF_2$	37.0	20	1.3250	1.289	24.36	24.68	37.92 1.91	38.12[c] 1.90[d]
$CF_2{=}CF{-}CH{=}\overset{CF_3}{C}{-}CH_3$	71.5	22	1.3531	1.350	28.98	30.50	37.91 2.12	37.72[c] 2.08[d]
$CF_2{=}CF{-}CH{=}CH{-}CF_3$	50.5	22	1.3322	1.389	24.36	26.01	34.11 1.15	33.90[c] 1.26[d]
$CF_2{=}CF{-}CH{=}CFCl$	53.0	24	1.3804	1.431	24.6	25.9	22.1	22.3 [e]

a. Previously reported by Miller (See reference 19)
b. Molecular weight
c. % carbon
d. % hydrogen
e. % chlorine

hydrochloric acid, conditions known to favor the replacement of iodine by hydrogen (10), the same compounds were obtained in approximately the same ratio. These reactions represent a novel synthetic procedure for the dehalogenation and reduction of a halogen compound in a single step.

The ease with which a number of these dienes were found to undergo polymerization offers a good indication of their value in the production of new polymers and elastomers. The straight chain structures containing both hydrogen and fluorine underwent polymerization at a much more rapid rate than did the branched chain compounds and the completely fluorinated butadienes. For example 1, 1, 2-trifluorobutadiene, 1, 1, 2, 4-tetrafluorobutadiene and 2-H-pentafluorobutadiene underwent spontaneous polymerization at room temperature when sealed in glass tubes, while the branched chain dienes generally required elevated temperatures and the aid of a catalyst for polymer formation.

In view of the important part played by 2-chlorobutadiene in present synthetic rubber, it was highly desirable to further test the fluorine analog, 2-fluorobutadiene, in connection with the present Arctic Rubber Program. As mentioned in a previous section of this dissertation, 2-fluorobutadiene was prepared earlier by Mochel and Salisbury (21). However, their procedure for the catalytic addition of anhydrous hydrogen fluoride to vinyl acetylene did not seem suitable as a laboratory method in view of the explosive nature of vinylacetylene and the exact conditions of control required to carry out the process. Attention was then turned toward a more convenient method of preparation that could be carried out in the laboratory. A series of reactions using butene-2 as a starting point was proposed as outlined by the following steps.

I. $CH_3CH{=}CHCH_3 + Cl_2 \dashrightarrow CH_3CHClCHClCH_3$

II. $CH_3CHClCHClCH_3 \xrightarrow{-\,HCl} CH_3CCl{=}CHCH_3$

III. $CH_3CCl{=}CHCH_3 + HF \dashrightarrow CH_3CFClCH_2CH_3$

IV. $CH_3CFClCH_2CH_3 + Cl_2 \dashrightarrow CH_3CFClCHClCH_3 +$

$CH_3CFClCH_2CH_2Cl$

V. $$\left.\begin{array}{l} CH_3CFClCHClCH_3 \\ \\ CH_3CFClCH_2CH_2Cl \end{array}\right\rangle \xrightarrow{-2\ HCl} CH_2{=}CF{-}CH{=}CH_2.$$

These reactions employ standard procedures that can be readily carried out using available laboratory equipment.

The chlorination of butene-2, as in step I, was carried out in the liquid phase by bubbling chlorine gas into the condensed butene held at a temperature of - 20° or lower. The yields were in the order of 90% and it was possible to use the resulting 2, 3-dichlorobutane without further purification. The second step of the synthesis was satisfactorily carried out using alcoholic potassium hydroxide in the conventional manner to give good yields of 2-chlorobutene-2. The fluorination reaction indicated by Step III was carried out in a stainless steel autoclave at room temperature using anhydrous hydrogen fluoride. A mixture of products resulted of which the desired 2-chloro-2-fluorobutane was the major component. Approximately equal molar ratios of 2, 2-dichlorobutane and 2, 2-difluorobutane were obtained as the result of an apparent disproportionation reaction involving the 2-chloro-2-fluorobutane.

In order to obtain the desired diene structure, it was necessary to prepare a precursor from which the double elimination of hydrogen halide could be effected. With this in mind 2-chloro-2-fluorobutane was subjected to a chlorination in the presence of ultraviolet radiation as shown by reaction IV of the above series. This photochemical substitution of hydrogen atoms by chlorine resulted in the formation of two isomeric dichloro compounds, 2, 3-dichloro-2-fluorobutane and 2, 4-dichloro-2-fluorobutane, in approximately equal molar ratio. Both of these isomers offer possible routes to 2-fluorobutadiene through elimination of two hydrogen chloride molecules.

The conversion of the dichlorofluorobutane isomers to 2-fluorobutadiene at first offered some difficulty in that two molecules of hydrogen chloride could not be eliminated from either of the two isomers using the conventional methods. Treatment with aqueous and alcoholic solutions of potassium hydroxide gave only a butene derivative by elimination of a single hydrogen chloride molecule. When an attempt was made to dehydrochlorinate 2, 4-dichloro-2-fluorobutane using fused potassium hydroxide, a small amount of 2-fluorobutadiene was formed; however, a surface coating of potassium chloride soon covered the hydroxide rendering it inactive to further dehydrochlorination.

The investigation was then directed toward a thermal dehydrochlorination, since it is known (14) that removal of hydrogen chloride from certain chlorofluoroethanes can be accomplished by passing the vapors through a tube heated to temperatures of 500 to 600° . It was found that only the monoölefin was obtained when the vapors of 2, 3-dichloro-2-fluorobutane or 2, 4-dichloro-2-fluorobutane were passed through a Pyrex tube containing Berl saddles at a temperature of 550° . However, when the tube was packed with granulated soda lime, conversion to the 2-fluorobutadiene occurred readily at a temperature of 400° . At temperatures above 400° carbonization of the starting material became noticeable and the conversion to the 2-fluorobutadiene was decreased. Both of the dichlorofluorobutanes were converted to 2-fluorobutadiene and to approximately the same extent. The conversion to the diene was of the order of 30-40% for average runs.

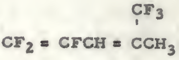
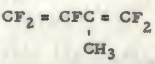
Several interesting observations have been made for the infrared absorption spectra of the various fluorine substituted olefins and dienes prepared in this research. The double bond absorption maxima for these olefins and dienes are listed in Table V. The influence of fluorine substitution in olefins on the infrared absorption spectra has been observed by a number of workers (1) and a general shift of the carbon-carbon double bond stretching vibration toward shorter wave lengths has been noticed. There have been few attempts made however, to assign absorption bands to specific configurations of the fluoroölefin structures. It is believed that sufficient data are available from compounds prepared in this research and in the previous research of Lovelace (17) to warrant the assignment of certain groups. An examination of the spectroscopic data given in Table V clearly illustrates the definite shift of the carbon-carbon double bond absorption toward shorter wave lengths as the number of fluorine atoms attached to the carbon atoms constituting the double bond increases.

When the carbon atoms of the double bond contain no fluorine atoms, for instance configurations of the types $CH_2=CH-$, $CH_2=C(CH_3)-$ and $(CH_3)_2C=CH-$, absorption for the carbon-carbon double bond stretch occurs in the range of 6.03 to 6.08 microns. This is illustrated for a number of compounds having such groups listed in the following table.

Compounds having a fluorine on a terminal carbon atom of the double bond, as in the $CHF=CH-$ group, show maximum absorption for the $C=C$ stretch at 5.94 or 5.95 microns, a shift of about 0.1 micron from the absorption maxima of the corresponding hydrocarbon group.

TABLE V

INFRARED ABSORPTION MAXIMA FOR THE C = C STRETCH OF OLEFINS AND DIENES CONTAINING FLUORINE

Compound	W. Length in microns	Compound	W. Length in microns
$CH_2 = CHCF_2Cl$*	6.03	$CF_2 = CFCF_2Br$*	5.60
$CH_2 = CHCF_2Br$*	6.07	$CF_2 = CFCFClCF_2Cl$	5.60
$CH_2 = CHCFClCF_2Br$	6.07	$CF_2 = CFCH_2CH_3$	5.59
$CH_2 = C(CH_3)CH_2CF_2Cl$*	6.07	$CF_2 = CFCH_2CH_2Br$	5.59
$(CH_3)_2C = CHCCl_3$*	6.08	$CF_2 = CFCH = CH_2$	5.58 5.66
$CHF = CHCF_2Br$*	5.95	$CF_2 = CFCH = CHF$	5.61 6.00
$CHF = CHCFClCF_2Br$	5.94		
$CFCl = CHCFClCF_2Cl$	5.91	$CF_2 = CFCH = CFCl$	5.65 6.02
$CF_3CH = CHCFClCF_2Cl$	5.91	$CF_2 = CFCH = CF_2$	5.58 5.78
$CH_3(CF_3)C = CHCFClCF_2Cl$	5.91		
$CF_2 = C(CH_3)CFClCF_2Cl$	5.73	$CF_2 = CFCF = CF_2$	5.55 5.64
$CF_2 = CHCH(CH_3)CH_3$*	5.72	$CF_2 = CFCH = CHCF_3$	5.68 6.00
$CF_2 = CHCH(CH_3)CH_2Cl$*	5.70		
$CF_2 = CHCF_2CH_2CF_2Br$*	5.70	 $CF_2 = CFCH = \overset{CF_3}{C}CH_3$	5.71 5.80
$CF_2 = CHCF_2Br$*	5.70		
$CF_2 = CHCFClCF_2Br$	5.67	 $CF_2 = CF\underset{CH_3}{C} = CF_2$	5.59 5.74
$CF_2 = CHCF_3$	5.65		

* Compounds prepared by Lovelace (see reference 17)

It is interesting also to observe that replacement of a hydrogen atom on a vinyl group by a trifluoromethyl group exerts approximately the same qualitative effect on the carbon-carbon double bond as does a fluorine atom. For example, the compounds $CF_3CH{=}CHCFClCF_2Cl$ and $CH_3C(CF_3){=}CHCFClCF_2Cl$ both show maximum absorption at 5.91 microns, while the compound $CHF{=}CHCFClCF_2Br$ absorbs at 5.94 microns. The presence of a chlorine atom on the terminal carbon of the $CHF{=}CH$- group has only a small effect on the double bond absorption. Thus the compound $CFCl{=}CHCFClCF_2Cl$ absorbs at 5.91 microns.

A greater shift in the $C{=}C$ stretching vibration is noticed when two fluorine atoms are located on the terminal carbon atom of the double bond. Several olefins are listed in Table V that have the $CF_2{=}CH$- configuration and all show carbon-carbon double bond absorption in the range of 5.65 to 5.73 microns. For compounds containing the perfluorovinyl group, $CF_2{=}CF$-, maximum absorption is observed at 5.59 and 5.60 microns for the double bond stretching vibration.

No attempt to adjust the assignments discussed above to the series of conjugated dienes is to be made at this time. It is known (1) that the effect of conjugation on the carbon-carbon double bond absorption is to shift the band toward $\overset{?}{\text{shorter}}$ wavelengths. In addition, double absorption maxima are characteristic of a conjugated system due to the in-phase and out-of-phase stretching vibrations. The dienes listed in the accompanying table exhibit the expected double absorption maxima in all cases accompanied by a shift in the direction of shorter wavelengths. The combined effect of the substituted fluorine atoms and that of the conjugated system make it extremely difficult to predict qualitative shifts in the region of the carbon-carbon double bond stretching vibration. All of the dienes listed in Table V contain the perfluorovinyl group and it is of some interest to note that with few exceptions, an absorption band occurs within the range of 5.55 to 5.65 microns which varies little from 5.59 to 5.60 microns assigned to the perfluorovinyl group of the monoölefins.

GENERAL CONSIDERATIONS

All temperatures reported in this dissertation are on the centigrade scale and are uncorrected. The distillations were carried out using a vacuum jacket silvered column for materials boiling below room temperature and either a 45 cm. or 20 cm. electrically heated jacketed column packed with one-eighth inch glass helices for the higher boiling materials. Pressures during distillation under 10 mm. were determined by a McLeod gauge, pressures above 10 mm. were read from a Zimmerli gauge.

Refractive indices were determined with an Abbe refractometer at the temperatures indicated. Densities were determined at the temperatures indicated using a one ml. pycnometer calibrated against water at 25° C. and corrected to water at 4° C. Molar refractions were calculated using the Lorenz-Lorentz equation. The values for the atomic refractions were taken from Lange's "Handbook of Chemistry" sixth edition p. 1025. In all cases the value 1.1000 was used for the atomic refraction of fluorine. No correction was made for exhaltation due to conjugated double bonds. Since all such compounds described in this dissertation contained varying numbers of fluorine atoms per molecule, a constant exhaltation value would have little significance.

The infrared spectra were obtained by a Perkin-Elmer Model 21 double beam, recording, infrared spectrophotometer.

The autoclaves used in this research were obtained from the American Instrument Company. The organic peroxides were obtained from the Lucidol Division, Novadel-Agene Corporation.

All analyses were carried out by Peninsular ChemResearch, Inc., Gainesville, Florida. Molecular weights were determined for gaseous products by the vapor density method.

The reactants used in this research were purchased whenever available. The materials, other than the common laboratory stock chemicals, with the sources of supply are listed below. Reactants not commercially available were prepared in the laboratory by procedures described in a later section of this dissertation.

1. Chlorotrifluoroethylene	General Chemical Division, Allied Chemical and Dye Corp.
2. Fluoroethylene	Organic Chemicals Department, E. I. duPont de Nemours and Company
3. 1, 1-Difluoroethylene	General Chemical Division, Allied Chemical and Dye Corp.
4. Ethylene	The Matheson Company

5. Iodine monochloride	Distillation Products Industries, Division of Eastman Kodak Company
6. Perfluorobutyric acid.	Minnesota Mining and Mfg. Company

III EXPERIMENTAL

In general all addition reactions were carried out in either a one and four-tenths liter or a three-tenths liter stainless steel reaction vessel fitted with a valve, pressure gauge and blow-out assembly. The method of loading was dependent upon the properties of the olefin. Those olefins boiling sufficiently high to be condensed at the temperature of Dry-Ice and acetone were collected in a cold trap, weighed and poured into the precooled reaction vessel containing the addendum and catalyst. The vessel was then sealed and rocked at the desired temperature. In the case of olefins which could not be condensed by Dry-Ice and acetone, the procedure was somewhat modified. The autoclave was charged with the appropriate addendum and catalyst and sealed. The olefin was introduced through the valve and gauge assembly under the pressure of the cylinder, the weight of olefin being determined by difference in cylinder weight. After the heating and rocking process, the reaction vessel was cooled in ice water and any unreacted olefin was vented into a cold trap immersed in Dry-Ice and acetone and weighed. The autoclave was then opened and the resulting liquid material subjected to fractional distillation.

A. Additions of 1, 2-Dibromo-2-chloro-1, 1, 2-trifluoroethane to Olefins

1. Ethylene

The autoclave was charged with 1125 g. (4.0 moles) of 1, 2-dibromo-2-chloro-1, 1, 2-trifluoroethane, 52 g. (1.9 moles) of ethylene and 15 g. (0.06 mole) of benzoyl peroxide. It was sealed, heated and rocked four hours at 100°. After the vessel was cooled in ice water, the excess ethylene was vented and the liquid reaction product was distilled. There was obtained 319 g. of the one-to-one adduct, $CF_2BrCFClCH_2CH_2Br$, for which the following constants were obtained: b.p. 67.4° /20 mm., n_D^{25} 1.4563, d_4^{25} 2.035, MR_D calculated for $C_4H_4Br_2ClF_3$: 41.08, found: 40.67. Analysis; silver equivalent calculated for $C_4H_4Br_2ClF_3$: 101.5, found: 101.9. The conversion to $CF_2BrCFClCH_2CH_2Br$ was 58% based on the ethylene.

This compound must have the structure $CF_2BrCFClCH_2CH_2Br$, since the radical $CF_2BrCFCl\cdot$ produced by the rupture of the carbon-bromine bond of the $-CFClBr$ group, as discussed in the previous section, adds to the symmetrical ethylene molecule to give the radical $CF_2BrCFClCH_2CH_2\cdot$ which obtains a bromine atom from a second molecule of $CF_2BrCFClBr$.

2. Fluoroethylene

In the manner described above 1125 g. (4 moles) of 1, 2-dibromo-2-chloro-1, 1, 2-trifluoroethane, 60 g. (1. 3 moles) of fluoroethylene and 10 g. (0. 04 mole) of benzoyl peroxide were charged into the reaction vessel. The vessel was sealed, heated and rocked four hours at 100°. It was then cooled, opened and the unreacted 1, 2-dibromo-2-chloro-1, 1, 2-trifluoroethane was removed by distillation. The high boiling liquid remaining was fractionated under vacuum giving two fractions.

The lower boiling fraction, 311 g., contained the one-to-one adduct, $CF_2BrCFClCH_2CHFBr$, with the following constants: b. p. 72° /32 mm., n_D^{25} 1. 4405, d_4^{25} 2. 075, MR_D calculated for $C_4H_3Br_2ClF_4$: 41. 08, found: 41. 00. Analysis; silver equivalent calculated for $C_4H_3Br_2ClF_4$: 107. 4, found: 106. 5. The conversion to the one-to-one adduct was 74% based on the fluoroethylene. This compound was assigned the structure $CF_2BrCFClCH_2CHFBr$, since it has been shown by Lovelace (17) that in an analogous reaction dibromodifluoromethane and fluoroethylene gave 1, 3-dibromo-1, 1, 3-trifluoropropane.

The higher boiling fraction, 34 g., contained the two-to-one addition product, $CF_2BrCFClCH_2CHFCH_2CHFBr$, with the following properties: b. p. 104. 5/15 mm., n_D^{27} 1. 4428, d_4^{27} 1. 946, MR_D calculated for $C_6H_6Br_2ClF_5$: 50. 30, found: 50. 13. Analysis; silver equivalent calculated for $C_6H_6Br_2ClF_5$: 122.8, found: 122.7. The conversion to two-to-one adduct was 6.4% based on fluoroethylene. The structure $CF_2BrCFClCH_2CHFCH_2CHFBr$ was assigned to this compound for the reasons discussed in the previous section.

3. 1,1-Difluoroethylene

In the manner previously described 1073 g. (3.9 moles) of 1,2-dibromo-2-chloro-1,1,2-trifluoroethane, 122 g. (1.9 moles) of 1,1-difluoroethylene and 15 g. (0.06 mole) of benzoyl peroxide were reacted at 100° for four hours. Fractional distillation of the resulting liquid material gave 282 g., 44% conversion, of one-to-one adduct, and 123 g., 23.4% conversion of the two-to-one adduct.

For the one-to-one adduct the following constants were obtained: b.p. 70.1°/50 mm., n_D^{27} 1.4230, d_4^{27} 2.063, MR_D calculated for $CF_2BrCFClCH_2CF_2Br$: 41.08, found: 41.03. Analysis; silver equivalent calculated for $C_4H_2Br_2ClF_5$: 113.4, found: 111.9. The structure of this compound must be $CF_2BrCFClCH_2CF_2Br$ since treatment with a strong base eliminates hydrogen bromide.

The following constants were obtained for the two-to-one adduct: b.p. 90-91°/20 mm., n_D^{27} 1.4112, d_4^{27} 2.014, MR_D calculated for $C_6H_4Br_2ClF_7$: 49.61, found: 50.30. Analysis; silver equivalent calculated for $C_6H_4Br_2ClF_7$: 134.7, found: 133.6. The two-to-one adduct was assigned the structure $CF_2BrCFClCH_2CF_2CH_2CF_2Br$ for reasons discussed previously.

4. Trifluoroethylene

As described above 1,2-dibromo-2-chloro-1,1,2-trifluoroethane 1125 g. (4 moles), trifluoroethylene 94 g. (1.15 moles) and benzoyl peroxide 15 g. (0.06 mole) were reacted for four hours at 100°. Fractional distillation of the resulting liquid material gave 4 g. of unreacted trifluoroethylene, 957 g. recovered $CF_2BrCFClBr$, 58 g., a 16.2% conversion of the one-to-one adduct, 52 g., a 20% conversion of the two-to-one adduct and higher molecular weight addition products that were not isolated.

The one-to-one adduct had the following constants: b.p. 61.5°/40 mm., n_D^{23} 1.4330, d_4^{23} 2.013, MR_D calculated for $C_4HBr_2ClF_6$: 41.07, found: 46.27. Analysis; silver equivalent calculated for $C_4HBr_2ClF_6$: 116.1, found: 116.4. This adduct must have the structure $CF_2BrCFClCHFCF_2Br$ since treatment by a base eliminated hydrogen bromide.

The two-to-one addition product had the following constants: b.p. 79.5°/15 mm., n_D^{25} 1.3943, d_4^{25} 2.077, MR_D calculated for $C_6H_2Br_2ClF_9$: 50.31, found: 50.75. Analysis; silver equivalent calculated for $C_6H_2Br_2ClF_9$: 146.8, found: 147.0. For the reasons previously discussed, this compound has been assigned the structure $CF_2BrCFClCHFCF_2CHFCF_2Br$.

5. 1, 1-Difluoropropene-1

In the manner described a reaction vessel was charged with 370 g. (1.36 moles) of 1, 2-dibromo-2-chloro-1, 1, 2-trifluoroethane, 26 g. (0.33 mole) of 1, 1-difluoropropene-1 and 5 g. (0.02 mole) of benzoyl peroxide, heated and rocked four hours at 100°. Fractional distillation of the resulting material gave 22.5 g. of recovered difluoropropene, 334 g. of unreacted $CF_2BrCFClBr$ and 25 g. of solid residue. No simple addition product was obtained.

6. 1-Chloro-1-fluoroethylene

As described above a reaction vessel was charged with 1181 g. (4.3 moles) of 1, 2-dibromo-2-chloro-1, 1, 2-trifluoroethane, 98 g. (1.17 moles) of 1-chloro-1-fluoroethylene and 15 g. (0.06 mole) of benzoyl peroxide, heated and rocked four hours at 100°. After removing the excess $CF_2BrCFClBr$, 1110 g. there remained 137 g. of a solid material that was assumed to be a polymer of chlorofluoroethylene containing some 1, 2-dibromo-2-chloro-1, 1, 2-trifluoroethane. None of the desired addition product was obtained.

B. Additions of 1,2-Dichloro-2-iodo-1,1,2-trifluoroethane to Olefins

1. Trifluoroethylene

In the manner previously described the autoclave was charged with 356 g. (1.28 moles) of 1,2-dichloro-2-iodo-1,1,2-trifluoroethane, 38 g. (0.46 mole) of trifluoroethylene and 5 g. (0.02 mole) of benzoyl peroxide. It was heated and rocked four hours at 100°. The 425 g. of resulting liquid material was fractionally distilled to give 263 g. of unreacted $CF_2ClCFClI$ and 132 g. of the one-to-one adduct, $CF_2ClCFClCHFCF_2I$, having the following properties: b.p. 56.0/23 mm., n_D^{28} 1.4224, d_4^{28} 2.110, MR_D calculated for $C_4HCl_2F_6I$: 43.21, found: 43.49. Analysis; silver equivalent calculated for $C_4HCl_2F_6I$: 120.3, found: 120.0. The conversion to the one-to-one adduct was 79% based on trifluoroethylene. This compound must have the structure $CF_2ClCFClCHFCF_2I$ since treatment with a base caused the elimination of hydrogen iodide from the compound.

2. 1-Chloro-1-fluoroethylene

In the usual manner a reaction vessel was charged with 375 g. (1.35 moles) of 1,2-dichloro-2-iodo-1,1,2-trifluoroethane, 35 g. (0.44 mole) of 1-chloro-1-fluoroethylene and 5 g. (0.02 mole) of benzoyl peroxide, heated and rocked four hours at 100°. Fractional distillation of the 409 g. of liquid material obtained gave 276 g. of unreacted $CF_2ClCFClI$, 71 g., 45% conversion, of one-to-one addition product and 44 g. of a high boiling residue which could not be identified.

The one-to-one adduct had the following constants: b.p. 70°/13 mm., n_D^{22} 1.4741, d_4^{22} 2.075, MR_D calculated for $C_4H_2Cl_3F_4I$: 48.07, found: 48.68. Analysis; silver equivalent calculated for $C_4H_2Cl_3F_4I$: 89.8, found: 90.0. This compound was assigned the structure $CF_2ClCFClCH_2CFClI$ since it readily loses hydrogen iodide when treated with a base.

3. Chlorotrifluoroethylene

The reaction of 1390 g. (5 moles) of 1,2-dichloro-2-iodo-1,1,2-trifluoroethane, 117 g. (1 mole) of chlorotrifluoroethylene and 15 g. (0.06 mole) of benzoyl peroxide in the manner previously described yielded on distillation, 1233 g. of unreacted $CF_2ClCFClI$, 102 g. (26%) of the one-to-one adduct b. 70-79°/24 mm. and 150 g. of a high boiling viscous residue which was not further identified. A center cut of the one-to-one addition product had the following constants: b.p. 74.0/24 mm., n_D^{22} 1.4405, d_4^{22} 2.182, MR_D calculated for $C_4Cl_3F_6I$: 48.21, found: 47.8. Miller (20) previously prepared this adduct by the same procedure and showed it to have the structure $CF_2ClCFClCF_2CFClI$.

4. 1, 1-Difluoropropene-1

In the manner described the reaction vessel was charged with 323 g. (1.12 moles) of 1, 2-dichloro-2-iodo-1, 1, 2-trifluoroethane, 17 g. (0.22 mole) of 1, 1-difluoropropene-1 and 5 g. (0.02 mole) of benzoyl peroxide heated and rocked four hours at 100°. Fractional distillation of the reaction product gave 238 g. of unreacted $CF_2ClCFClI$ and 70 g. of the one-to-one adduct. The conversion to the adduct was 89% based on 1, 1-difluoropropene-1.

The following constants were obtained for this adduct: b.p. 75.0° /20 mm., n_D^{25} 1.4567, d_4^{25} 1.994, MR_D calculated for $C_5H_4Cl_2F_5I$: 47.82, found: 48.72. Analysis; silver equivalent calculated for $C_5H_4Cl_2F_5I$: 118.97, found: 119.2. This compound must have the structure $CF_2ClCFClC(CH_3)HCF_2I$ since it readily loses hydrogen iodide on treatment with a base and chlorine when treated with zinc to form a conjugated diene.

5. 3, 3, 3-Trifluoropropene-1

In the usual manner an autoclave was charged with 406 g. (1.45 moles) of 1, 2-dichloro-2-iodo-1, 1, 2-trifluoroethane, 40 g. (0.417 mole) of 3, 3, 3-trifluoropropene-1 and 5 g. (0.02 mole) of benzoyl peroxide, heated and rocked four hours at 100°. The reaction product, 444 g. was fractionally distilled to give 261 g. of recovered $CF_2ClCFClI$ and 150 g. of one-to-one addition product representing a 95% conversion to the adduct based on the trifluoropropene. The constants for this compound are as follows: b.p. 61° /18 mm., n_D^{22} 1.4275, d_4^{22} 2.013, MR_D calculated for $C_5H_3Cl_2F_6I$: 47.82, found: 47.91. Analysis; silver equivalent calculated for $C_5H_3Cl_2F_6I$: 125.0, found: 125.9. This compound was assigned the structure $CF_2ClCFClCH_2CHICF_3$ on the basis that addition of the carbon containing radical takes place preferentially at the terminal methylene group (8) (17).

6. 2-Trifluoromethylpropene

In the manner described previously 350 g. (1.25 moles) of 1,2-dichloro-2-iodo-1,1,2-trifluoroethane, 37 g. (0.33 mole) of 2-trifluoromethylpropene and 5 g. (0.02 mole) of benzoyl peroxide were reacted to give 113 g., 87% conversion, of the one-to-one addition product with the following constants: b.p. 65.5° /12 mm., n_D^{22} 1.4418, d_4^{22} 1.947, MR_D calculated for $C_6H_5Cl_2F_6I$: 52.45, found: 52.84. Analysis; silver equivalent calculated for $C_6H_5Cl_2F_6I$: 129.64, found: 129.2. This compound was assigned the structure $CF_2ClCFClCH_2C(CF_3)ICH_3$, since it readily loses hydrogen iodide when treated with a base.

7. 2-H-Pentafluoropropene

In the manner described the autoclave was charged with 350 g. (1.25 moles) of 1,2-dichloro-2-iodo-1,1,2-trifluoroethane, 35 g. (0.26

mole) of 2-H-pentafluoropropene and 5 g. (0.02 mole) of benzoyl peroxide, heated and rocked four hours at 100°. Fractional distillation of the resulting liquid material gave 29 g. of unreacted $CF_2=CHCF_3$ and 345 g. of $CF_2ClCFClI$. No simple addition product was formed.

Similar results were obtained when the reaction was repeated at 150° using di-t-butyl peroxide as the catalyst.

8. Perfluoropropene

In the manner described above 407 g. (1.46 moles) of 1,2-dichloro-2-iodo-1,1,2-trifluoroethane, 40 g. (0.29 mole) of perfluoropropene and 5 g. (0.02 mole) of benzoyl peroxide were reacted. The autoclave was cooled and the gases bled into a trap cooled in a Dry Ice-acetone mixture giving 36 g. of unreacted perfluoropropene. The unreacted $CF_2ClCFClI$ was stripped off the remaining liquid material to leave 24 g. of high boiling residue. This was further distilled to give a fraction (5 g.) of material b. 45-54° /18 mm. and 15 g. of tarry residue. No further attempt was made to identify this material.

C. Preparation of Olefins and Dienes from the Addition Products

1. 4-Bromo-3-chloro-4, 4, 3-trifluorobutene-1

A saturated solution of potassium hydroxide, 3 moles, in propanol-1, 1000 ml., was added dropwise to 305 g. (1 mole) of hot 1, 4-dibromo-2-chloro-1, 1, 2-trifluorobutane contained in a two liter flask equipped with a stirrer, addition funnel and a variable take-off distilling head. A mixture of the olefin and propanol was distilled off as the reaction proceeded. This material was washed well with water and dried. Fractional distillation of the dried product gave 150 g. of the olefin, $CH_2=CHCFClCF_2Br$, for a 68% conversion.

The following constants were obtained for this compound: b.p. 99.5°, n_D^{25} 1.4092, d_4^{25} 1.678, MR_D calculated for $C_4H_3BrClF_3$: 32.84, found: 32.93. Analysis; silver equivalent calculated for $C_4H_3BrClF_3$: 111.7, found: 113.4. This olefin must have the structure $CF_2BrCFClCH=CH_2$ since potassium bromide was obtained from the above reaction. The infrared absorption spectrum for this olefin shows a strong absorption band at 6.07 microns which is characteristic of the ethylenic linkage.

2. 1, 1, 2-Trifluorobutadiene-1, 3

The above olefin, 224 g. (1 mole) was added dropwise to a refluxing mixture of 2 moles of zinc dust, 1 g. of zinc chloride and 200 ml.

of propanol-2. The product, 1, 1, 2-trifluorobutadiene-1, 3, was collected as it was formed in a trap immersed in Dry Ice and acetone. Distillation of the 110 g. of crude product gave a fraction of 95 g., 88% conversion, of the pure diene: b.p. 7.8-8.0°. Analysis; molecular weight calculated for $C_4H_3F_3$: 108.1, found: 109.5. These values agree with those previously reported by Lovelace (17) for the same compound prepared by a different method. The infrared absorption spectrum showed strong absorption bands at 5.58 and 5.66 microns for the conjugated system.

3. 3-Bromo-3-chloro-1, 3, 4, 4-tetrafluorobutene-1

To a hot aqueous solution of 150 g. of potassium hydroxide in 100 ml. of water was added dropwise one mole (323 g.) of 1, 4-dibromo-2-chloro-1, 1, 2, 4-tetrafluorobutane. The product was distilled from the reaction flask as it formed, washed with water and dried. Fractional distillation gave 65 g. of the desired olefin and 38.5 g. of the unreacted butane for a yield of 48%.

The $CHF=CHCFClCF_2Br$ had the following constants: b.p. 97-97.3°, n_D^{25} 1.3961, d_4^{25} 1.781, MR_D calculated: 32.44, found: 32.58. Analysis; silver equivalent calculated for $C_4H_2BrClF_4$: 120.7, found: 121.3. The infrared spectrum shows an absorption band at 5.93 microns for the unsaturated linkage.

4. 1, 1, 2, 4-Tetrafluorobutadiene-1, 3

Treatment of the above olefin (160 g., 0.66 mole) with a slurry of 75 g. of zinc dust in 80 ml. of propanol-1 contained in a 200 ml., three neck flask equipped with a stirrer, addition funnel and a variable take-off distilling head resulted in 74 g. of crude product. This was fractionally distilled to give 67 g. of the 1, 1, 2, 4-tetrafluorobutadiene-1, 3 b. 16-18° for a conversion of 80%.

A center cut of this material had the following constants: b.p. 16.5°, n_D^0 1.3427, d_4^0 1.342, MR_D calculated for $C_4H_2F_4$: 19.74, found: 19.84. Analysis; molecular weight calculated for $C_4H_2F_4$: 126.1, found: 122.8. Infrared absorption bands occurred at 5.62 and 6.00 microns for the unsaturated linkages.

5. 4-Bromo-3-chloro-1, 1, 3, 4, 4-pentafluorobutene-1

The addition product of 1, 2-dibromo-2-chloro-1, 1, 2-trifluoroethane and 1, 1, -difluoroethylene, $CF_2BrCFClCH_2CF_2Br$, 170 g. (0.5 mole) was added dropwise to a hot solution of potassium hydroxide, 100 g., in 75 ml. of water. The crude product was distilled from the reaction flask as it formed, washed with water and dried. Fractional distillation of the 111 g. of material thus obtained gave 63 g., 48.8% conversion, of the desired 4-bromo-3-chloro-1, 1, 3, 4, 4-pentafluorobutene-1 with the following constants: b.p. 91.0°, n_D^{24} 1.3837, d_4^{24} 1.838, MR_D calculated for $C_4HBrClF_5$: 32.84, found: 32.97.

Analysis; silver equivalent calculated for $C_4HBrClF_5$: 129.7, found: 130.2. The double bond absorption peak occurred at 5.72 microns as shown by the infrared spectrum.

This compound must have the structure, $CF_2=CH-CFClCF_2Br$, since potassium bromide was formed in the above reaction.

6. 2-H-Pentafluorobutadiene-1, 3

The above olefin, 58 g. (0.22 mole) was dropped onto a refluxing slurry of 65 g. zinc dust and 1 g. of anhydrous zinc chloride in 75 ml. of propanol-2 in the usual manner. The diene distilled from the reaction flask as it formed and was collected in a Dry Ice cooled trap attached to the reflux condenser. Fractionation of the crude material gave 26 g., 80% conversion, pure 2-H-pentafluorobutadiene, b.p. 15.5°. Analysis; molecular weight calculated for C_4HF_5: 144.1, found: 145.2. Absorption in the infrared region showed bands at 5.58 and 5.78 microns for the unsaturated system.

This compound was assigned the structure $CF_2=CH-CF=CF_2$.

7. 3, 4-Dichloro-1, 1, 2, 3, 4, 4-hexafluorobutene-1

1, 2-Dichloro-4-iodo-1, 1, 2, 3, 4, 4-hexafluorobutane, 126 g. (0.35 mole) was refluxed with a solution of potassium hydroxide, 70 g., in 40 ml. of water as previously described. The olefin distilled from the reaction flask and was washed once with a solution of sodium thiosulfate, once with water and dried. Fractional distillation of the 70.5 g. thus obtained gave 50 g., 71.5% conversion of $CF_2=CFCFClCF_2Cl$ having the following constants: b.p. 65.5-67.0°, n_D^{22} 1.3440, d_4^{22} 1.615, MR_D calculated for $C_4Cl_2F_6$: 29.9, found: 30.5. The infrared spectrum of this compound shows an absorption band at 5.60 microns for the double bond linkage. These values are in good agreement with those previously reported by Miller (19) for the same compound.

8. Perfluorobutadiene

Treatment of the above 3,4-dichloro-1,1,2,3,4,4-hexafluorobutene-1, 40 g. (0.17 mole) with a refluxing mixture of 33 g. zinc dust, 1 g. anhydrous zinc chloride and 50 ml. of propanol-2 in the usual manner gave 25 g. of material. This was fractionated to give 20 g. of the perfluorobutadiene, b.p. 7.1-7.3° for a conversion of 73% of the theory. This is in agreement with the value reported by Miller (19) for the same compound.

This diene shows infrared absorption bands at 5.55 and 5.64 microns characteristic of the conjugated system.

9. 1,3,4-Trichloro-1,3,4,4-tetrafluorobutene-1

1,2,4-Trichloro-4-iodo-1,1,2,4-tetrafluorobutane, the adduct of $CF_2ClCFClI$ and $CH_2=CFCl$, 70 g. (0.02 mole) was refluxed with a solution of potassium hydroxide, 50 g. in 25 ml. of water for a period of three hours. The organic material was distilled, washed with cold water, dried and fractionated. There was obtained a fraction of 18 g., 39% conversion, of 1, 3, 4-trichloro-1, 3, 4, 4-tetrafluorobutene-1 with the following properties: b.p. 102.5°, n_D^{24} 1.3993, d_4^{24} 1.586, MR_D calculated for $C_4HCl_3F_4$: 34.81, found: 35.28. Analysis; % chlorine calculated for $C_4HCl_3F_4$: 45.96, found: 45.70. Infrared absorption spectrum shows a characteristic absorption band at 5.91 microns for the oleinic linkage.

This compound has been assigned the structure, $CFCl{=}CHCFClCF_2Cl$, since the above reaction produced potassium iodide.

10. 1-Chloro-1, 3, 4, 4-tetrafluorobutadiene-1, 3

The 1, 3, 4-trichloro-1, 3, 4, 4-tetrafluorobutene-1, 18 g. prepared as above was treated in the usual manner with a refluxing mixture of 13 g. zinc dust, 0.5 g. copper powder and 20 ml. of propanol-1. The product was distilled from the reaction flask, washed with cold water, dried and fractionated. There was obtained a fraction of 8.0 g., a 64% conversion, of the diene, $CFCl{=}CHCF{=}CF_2$, for which the following constants were obtained: b.p. 53.0°, n_D^{24} 1.3804, d_4^{24} 1.431, MR_D calculated for C_4HClF_4: 24.6, found: 25.9. Analysis; % chlorine calculated for C_4HClF_4: 22.1, found: 22.3. The infrared spectrum of this compound showed the characteristic double absorption peaks at 5.65 and 6.02 microns for the conjugated diene.

The structure $CFCl=CH-CF=CF_2$ was assigned to this compound.

11. 3, 4-Dichloro-2-methyl-1, 1, 3, 4, 4-pentafluorobutene-1

The reaction product of $CF_2ClCFClI$ and $CF_2=CHCH_3$, $CF_2ICH(CH_3)CFClCF_2Cl$, was added to a hot solution of 70 g. potassium hydroxide in 50 ml. of water as previously described. The crude olefin was distilled as it formed, washed with a solution of sodium thiosulfate to remove traces of iodine and dried. Fractional distillation gave 52 g., 57% conversion, of the desired 3, 4-dichloro-2-methyl-1, 1, 3, 4, 4-pentafluorobutene-1. The following constants were determined for this compound: b.p. 100.5°, n_D^{22} 1.3746, d_4^{22} 1.515, MR_D calculated for $C_5H_3Cl_2F_5$: 34.56, found: 34.64. Analysis; % chlorine calculated for $C_5H_3Cl_2F_5$: 31.3, found: 31.4. The double bond linkage showed a strong infrared absorption band at 5.73 microns.

This compound must have the structure $CF_2=C(CH_3)CFClCF_2Cl$, since potassium iodide was a product of the above reaction.

12. 2-Methyl-1, 1, 3, 4, 4-pentafluorobutadiene-1, 3

The above olefin, 41 g. (0.18 mole), was reacted in the usual manner with a mixture of 33 g. of zinc dust, 1 g. of anhydrous zinc chloride and 50 ml. of propanol-1. The product was washed, dried and fractionally distilled to give 21 g. of the desired 2-methyl-1, 1, 3, 4, 4-pentafluorobutadiene for a conversion of 74% of the theory. The constants obtained for this compound are as follows: b.p. 37.0°, n_D^{20} 1.3250, d_4^{20} 1.289, MR_D calculated for $C_5H_3F_5$: 24.36, found: 24.68. Analysis; % carbon calculated for $C_5H_3F_5$: 37.92, found: 38.12, % hydrogen calculated: 1.91, found: 1.90.

The infrared spectrum of this diene showed absorption bands at 5.59 and 5.74 microns for the unsaturated system.

The structure of this compound must be $CF_2{=}C(CH_3)CF{=}CF_2$.

13. 4, 5-Dichloro-1, 1, 1, 4, 5, 5-hexafluoropentene-2

The addition product of 1, 2-dichloro-2-iodo-1, 1, 2-trifluoroethane and 3, 3, 3-trifluoropropene-1, $CF_2ClCFClCH_2CHICF_3$, 96 g. (0.2 mole) was reacted with 60 ml. of an aqueous solution containing 100 g. of potassium hydroxide as described. Fractionation of the crude product gave 40 g. (63%) of $CF_3CH{=}CHCFClCF_2Cl$ with the following properties: b.p. 87.5°, n_D^{23} 1.3472, d_4^{23} 1.519, MR_D calculated for $C_5H_2Cl_2F_6$: 34.56, found: 34.78. Analysis; % chlorine calculated for $C_5H_2Cl_2F_6$: 28.75, found: 29.0. Infrared absorption occurred at 5.92 microns for the unsaturated linkage.

Potassium iodide was found to be a product of the above reaction, thus the compound was given the structure $CF_3CH{=}CHCFClCF_2Cl$.

14. 3,4-Di-H-hexafluoropentadiene-1,3

The olefin prepared above, $CF_3CH{=}CHCFClCF_2Cl$, 39.5 g. (0.16 mole) was reacted with zinc dust 30 g., anhydrous zinc chloride 0.5 g. and propanol-1 50 ml. as described previously. There was obtained 20 g., a 72% conversion, of 3,4-di-H-hexafluoropentadiene-1,3 with the following constants: b.p. 50.5°, n_D^{22} 1.3322, d_4^{22} 1.389, MR_D calculated for $C_5H_2F_6$: 24.36, found: 26.01. Analysis; % carbon calculated for $C_5H_2F_6$: 34.11, found: 33.90, % hydrogen calculated: 1.15, found: 1.26.

An infrared spectroscopic examination of this diene showed an absorption band at 5.68 microns which is characteristic of the perfluorovinyl group and a band at 6.00 microns for the carbon-carbon double bond containing hydrogen atoms attached to the carbon atoms of the double bond.

This compound has thus been assigned the structure $CF_2{=}CFCH{=}CHCF_3$.

15. 3,4-Dichloro-2-trifluoromethyl-3,4,4-trifluoropentene-2

In the manner described 1,2-dichloro-4-iodo-1,1,2-trifluoro-4-trifluoromethylbutane, the adduct of $CF_2ClCFClI$ and $CH_2{=}C(CF_3)CH_3$, 107 g. (0.275 mole) was treated with a solution of potassium hydroxide, 50 g. in 25 ml. of water. Fractionation of the resulting material gave 36 g. of unreacted $CF_2ClCFClCH_2C(CF_3)ICH_3$ and 28 g. (40%) of the pentene with the following properties: b.p. 109.5°, n_D^{20} 1.3675, d_4^{20} 1.485, MR_D calculated for $C_6H_4Cl_2F_6$: 39.18, found: 39.51. Analysis; % chlorine calculated for $C_6H_4Cl_2F_6$: 27.2, found: 26.9. The infrared absorption maximum occurred at 5.92 microns for the unsaturated linkage.

The structure $CH_3C(CF_3)=CHCFClCF_2Cl$ was assigned to this compound since it reacts readily with zinc to form a conjugated diene.

16. 1,1,2-Trifluoro-4-trifluoromethylpentadiene-1,3

Twenty-two grams (0.085 mole) of the $CH_3C(CF_3)=CHCFClCF_2Cl$ prepared above was reacted in the usual manner with 15 g. of zinc dust and 0.5 g. of anhydrous zinc chloride suspended in 20 ml. of propanol-1. Distillation of the reaction product gave one fraction of 11.5 g. (72% conversion) of 1,1,2-trifluoro-4-trifluoromethylpentadiene-1,3 with the following constants: b.p. 71.5°, n_D^{22} 1.3531, d_4^{22} 1.350, MR_D calculated for $C_6H_4F_6$: 28.98, found: 30.50. Analysis; calculated for $C_6H_4F_6$, % carbon: 37.91, % hydrogen: 2.12, found, % carbon: 37.72, % hydrogen: 2.08. The infrared spectrum of this compound showed the characteristic double absorption bands at 5.71 and 5.80 microns for the conjugated double bonds.

This compound has been assigned the structure $CF_2=CF-CH=C(CF_3)CH_3$.

17. 1, 1, 2-Trifluorobutene-1 and 4-Bromo-1, 1, 2-trifluorobutene-1

2-Chloro-1, 4-dibromo-1, 1, 2-trifluorobutane, 95 g. (0. 32 mole) was added slowly to a refluxing mixture of 65 g. zinc dust, 1 g. copper powder and 100 ml. of propanol-2 in the manner already described. The crude product was collected over a temperature range of 75-90°, washed well with ice-water and dried. Fractional distillation gave one fraction, 4. 0 g., of material b. 14-15° and a second fraction of 18 g. b. 88-97°.

An infrared spectroscopic examination of the low boiling fraction showed the presence of the perfluorovinyl group with a maximum absorption band at 5. 59 microns and indicated the presence of a saturated hydrocarbon group. It is well known that zinc in the presence of a polar solvent such as alcohol can abstract halogen atoms that are attached to adjacent carbon atoms to give a carbon-carbon double bond. It has also been reported (20) that this metal can lead to the substitution of a halogen atom by a hydrogen atom in certain instances. Thus the structure $CF_2=CFCH_2CH_3$ has been assigned to the compound contained in this fraction.

The higher boiling fraction showed the following constants: b.p. 95°, n_D^{22} 1. 4022, d_4^{22} 1. 660, MR_D calculated for $C_4H_4BrF_3$: 28. 0, found: 29. 1. Analysis; % bromine calculated for $C_4H_4BrF_3$: 42. 25, found: 42. 4. The infrared spectrum shows strong absorption for the perfluorovinyl group at 5. 59 microns. The compound has been assigned the structure $CF_2=CFCH_2CH_2Br$.

In a similar reaction 2-chloro-1, 4-dibromo-1, 1, 2-trifluorobutane, 137 g. (0.45 mole) was refluxed with 400 ml. of 1.5 N hydrochloric acid and 130 g. (2 moles) of zinc dust. The product was distilled from the reaction mixture, washed twice with cold water and dried. Fractionation of the 60 g. of material thus obtained gave one fraction of 7.5 g. b. 14-14.2° and a second fraction of 43.5 g. b. 90-98°. The infrared spectra of these fractions were identical to those obtained above for the corresponding fractions. The products of the reaction must therefore be $CF_2=CFCH_2CH_3$ and $CF_2=CFCH_2CH_2Br$.

D. The Preparation of 2-Fluorobutadiene-1, 3

The synthesis of 2-fluorobutadiene-1, 3 starting from butene-2 is outlined by the following series of reactions:

$$CH_3CH{=}CHCH_3 + Cl_2 \dashrightarrow CH_3CHClCHClCH_3$$

$$CH_3CHClCHClCH_3 + KOH/alc. \dashrightarrow CH_3CCl{=}CHCH_3 + KCl + H_2O$$

$$CH_3CCl{=}CHCH_3 + HF \dashrightarrow CH_3CFClCH_2CH_3$$

$$2\ CH_3CFClCH_2CH_3 + 2\ Cl_2 \dashrightarrow CH_3CFClCH_2CH_2Cl + CH_3CFClCHClCH_3 + 2\ HCl$$

$$\left.\begin{array}{l} CH_3CFClCH_2CH_2Cl \\ \\ CH_3CFClCHClCH_3 \end{array}\right\rangle \xrightarrow{NaOH} CH_2{=}CF\text{-}CH{=}CH_2 + 2\ HCl$$

1. Chlorination of Butene-2

Butene-2, 8 moles, was introduced into a three-liter, three-neck flask immersed in a Dry Ice-acetone bath and fitted with a stirrer, gas delivery tube and a Dry Ice-acetone cooled reflux condenser. The reaction flask was cooled to -30° and eight moles of chlorine were added at a rate of about 2 moles an hour. The reaction mixture was maintained at a temperature of -20° or lower during the chlorination process.

The crude product was washed, dried and distilled to give 909 g., 88% conversion, of the desired 2, 3-dichlorobutane.

2. Dehydrochlorination of 2, 3-Dichlorobutane

2, 3-Dichlorobutane, 432 g. (3. 4 moles) was added slowly to a refluxing mixture of 560 g. technical grade potassium hydroxide in one liter of methanol. The reaction mixture was refluxed for an additional forty-five minutes after the addition was complete. The content of the flask was poured into a four liter beaker half filled with cracked ice. The organic layer was separated, washed twice with cold water, dried and distilled to give 231 g., 70. 5% conversion, of 2-chlorobutene-2 b. 65-70°.

3. Addition of Hydrogen Fluoride to 2-Chlorobutene-2

An autoclave was charged with 470 g. (5. 2 moles) of 2-chlorobutene-2 and 105 g. (5. 25 moles) of anhydrous hydrogen fluoride, sealed and rocked eighteen hours without heating. The crude product was washed with water and the unreacted hydrogen fluoride neutralized with potassium carbonate. The organic layer was separated and dried.

A second run was made in the same manner using 600 g. (6. 6 moles) of 2-chlorobutene-2 and 150 g. (7. 5 moles) of anhydrous hydrogen fluoride. The crude material was combined with that of the previous run and fractionated giving 66. 5 g., (6. 45% conversion) of $CH_3CF_2CH_2CH_3$ (5) b. 31. 5-35°, 685 g., (52. 5% conversion) of

$CH_3CFClCH_2CH_3$ (12) b. 65-70° and 131 g., (8.74% conversion) of $CH_3CCl_2CH_2CH_3$ b. 101.5-102.5°.

4. Chlorination of 2-Chloro-2-fluorobutane

To a liter three-neck flask equipped with a stirrer, reflux condenser, gas additon tube and liquid temperature thermometer was added 553 g. (5 moles) of 2-chloro-2-fluorobutane. The flask was surrounded by an ice bath and an ultraviolet lamp focused on the reaction vessel. A cold trap containing 344 g. (4.85 moles) of liquid chlorine was attached to the gas addition tube and chlorine was bubbled into the reaction over a period of seven hours. The crude product was washed with a cold, dilute sodium hydroxide solution again with cold water and dried giving 663 g. of material.

A second run made in the same manner and using like quantities of material gave 662 g. of crude product. The combined material was fractionated resulting in 121 g. (11% recovery) of unreacted $CH_3CFClCH_2CH_3$ b. 65-70°, 427 g. (30% conversion) of $CH_3CFClCHClCH_3$ (18) b. 106-110°, 306 g. (22% conversion) of $CH_3CFClCH_2CH_2Cl$ (18) b. 62-65° /90 mm., and 92 g. of an unidentified material b. 80-92/90 mm., which was presumed to be fluorotrichlorobutane isomers.

5. Thermal Dehydrochlorination of Fluorodichlorobutanes

The apparatus used for the thermal dehydrohalogenation of the isomeric fluorodichlorobutanes, $CH_3CFClCHClCH_3$ and $CH_3CFClCH_2CH_2Cl$, consisted of a one-liter graduated addition funnel to serve as a reservoir for the reactant, a stainless steel bellows proportionating pump, an electrically heated vaporizer consisting of a liter flask fitted with an intake tube extending to the bottom of the flask and an exhaust tube leading to a horizontally mounted pyrex reactor tube one-inch in diameter and thirty-inches in length heated by a double unit electric combustion furnace. The reactor tube was fitted with a Pyrex thermocouple well extending twenty-four inches into the tube from the intake end and was packed with low moisture four to eight mesh soda lime. The exhaust end of the reactor led through a water cooled condenser into a receiving flask to which was attached a series of three traps immersed in a Dry Ice-acetone cooling mixture.

In a typical dehydrohalogenation run 153 g. (125 ml.) of 2,4-dichloro-2-fluorobutane was pumped from the reservoir into the vaporizer at the rate of 75 ml. per hour. The vapors passed into the reactor heated to a temperature of 400°. The effluent gases were condensed and collected in the receiver and traps. Distillation of the crude product gave 29 g. of 2-fluorobutadiene (21) b. 10.5-13°, for a 38% conversion, and 40 g. of the unreacted starting material.

In a similar run 318 g. (265 ml.) of 2, 3-dichloro-2-fluorobutane was passed at a rate of 50 ml. per hour into the reactor heated to a temperature of 400°. Distillation of the resulting material gave 59 g. (37% conversion) of 2-fluorobutadiene.

E. Preparation of Intermediates

1. 1,2-Dibromo-2-chloro-1,1,2-trifluoroethane

The 1,2-dibromo-2-chloro-1,1,2-trifluoroethane was prepared in yields of 90 to 98% by bubbling commercial chlorotrifluoroethylene into bromine until free bromine was no longer evident.

2. 1,2-Dichloro-2-iodo-1,1,2-trifluoroethane

In a reaction similar to the one above, chlorotrifluoroethylene was bubbled into technical grade iodine monochloride dissolved in Freon 113. The reaction mixture containing considerable free iodine was decanted, washed with a sodium thiosulfate solution until colorless, dried and distilled. Yields of 50 to 60% were obtained.

3. 1-Fluoro-1-chloroethylene

The 1-fluoro-1-chloroethylene used in this research was prepared according to the method described by Young (27) who used the following series of reactions:

$$CH_2{=}CCl_2 + Br_2 \text{ ------> } CH_2BrCCl_2Br$$

$$CH_2BrCCl_2Br + 1/3\,SbF_3 \text{ ------> } CH_2BrCFCl_2 + 1/3\,SbCl_3$$

$$CH_2BrCFCl_2 + Zn \text{ -------> } CH_2{=}CFCl + ZnBr_2$$

4. Trifluoroethylene

The trifluoroethylene was prepared by a modification of the procedure described by Park (22) and is represented by the following reaction:

$$CF_2{=}CFCl + HBr \xrightarrow{\hspace{3cm}} CF_2BrCHFCl$$

$$CF_2BrCHFCl + Zn \xrightarrow{\hspace{3cm}} CF_2{=}CHF$$

The reactor, a piece of black iron pipe one and one-half inches in diameter and three feet eight inches in length, was wrapped with asbestos paper and wound with nichrome resistance wire so as to give four 500 watt heating units. The wire was coated with sodium silicate and insulated with asbestos cloth. It was mounted vertically and fitted at the top with a rubber stopper containing a thermocouple well extending 30-inches into the reactor and two inlet tubes; the bottom was fitted with a stopper containing a single exhaust tube.

The catalyst, a mixture of 75% by volume of 4-10 mesh activated charcoal and 25% anhydrous calcium sulfate, was charged into the tube. It was activated by heating two hours at 200° and 10-20 mm. pressure.

The reactor was allowed to cool to 100° and the reactants, hydrogen bromide and chlorotrifluoroethylene, were metered into it at a rate of 0.067 mole per minute each over a period of three hours. The exhaust gases were collected in a receiver packed in ice having connected to it a trap immersed in Dry Ice. The crude product was washed with a solution of sodium carbonate and with water. Distillation gave 1258 g. (6.4 moles) of the desired 1-bromo-2-chloro-1,1,2-trifluoroethane for a conversion of 53% of the theory.

The above 1-bromo-2-chloro-1,1,2-trifluoroethane, 6.4 moles, was added over a period of six hours to a refluxing mixture of zinc dust, 8 moles, zinc chloride, 20 g., copper powder, 50 g. and methanol, 1200 ml. The trifluoroethylene distilled as it was formed into a receiver immersed in a Dry Ice-acetone mixture. The crude product was distilled through a calcium chloride tower and condensed in a Dry Ice cooled receiver. There was obtained 486 g. of trifluoroethylene for a conversion of 92.5% of the theory.

5. 1,1-Difluoropropene-1

The 1,1-difluoropropene-1 used in this research was prepared from 1,1,2-trichloropropane by the following series of reactions (13).

$$CHCl_2CHClCH_3 + KOH/alc. \dashrightarrow CCl_2{=}CHCH_3 + KCl + H_2O$$
$$CCl_2{=}CHCH_3 + 2HF \dashrightarrow CF_2ClCH_2CH_3 + HCl$$
$$CF_2ClCH_2CH_3 + KOH/alc. \dashrightarrow CF_2{=}CHCH_3 + KCl + H_2O$$

To 1150 g. (7.8 moles) of hot 1,1,2-trichloropropane contained in a three-liter, three-neck flask equipped with a stirrer, addition funnel and a variable take-off distilling head was added a solution of potassium hydroxide, 600 g. in 1500 ml. of propanol-1. The crude product, distilling from the reaction flask as it formed, was washed with water, dried and distilled to give 680 g. (79%) of the desired 1, 1-dichloropropene-1 b. 74-78°.

The autoclave was cooled and charged with 680 g. (6.1 moles) of 1, 1-dichloropropene-1 and 320 g. (16 moles) of anhydrous hydrogen fluoride. It was sealed, heated and rocked four hours at 150°. The content was neutralized with a cold dilute potassium hydroxide solution, steam distilled and fractionated to give 353 g. (41%) of 1-chloro-1, 1-difluoropropane b. 25-29°.

1-Chloro-1, 1-difluoropropane, 353 g. (3 moles) was reacted with a solution of potassium hydroxide, 500 g. in one liter of ethanol in the usual manner. There was obtained 110 g. of the desired 1, 1-difluoropropene-1, b. -23 to -20° (13) and 124 g. of unreacted chlorodifluoropropane for a conversion of 47%.

6. 1, 1, 1-Trifluoropropene-2

The 1, 1, 1-trifluoropropene-2 was prepared from dibromodifluoromethane and ethylene by the series of reactions shown below:

$$CF_2Br_2 + CH_2{=}CH_2 \text{ -------> } CF_2BrCH_2CH_2Br \qquad (17).$$

$$CF_2BrCH_2CH_2Br + HF + SbCl_5 \text{ -------> }$$

$$CF_3CH_2CH_2Br + HBr \qquad (4).$$

$CF_3CH_2CH_2Br + KOH/alc. \dashrightarrow CF_3CH{=}CH_2$

The autoclave was charged with 500 g. of dibromodifluoromethane, 200 ml. of water and 15 g. of benzoyl peroxide. It was sealed and ethylene was introduced to a pressure of 400 p. s. i. The vessel was heated and rocked four hours at 100° ; the excess gases were released and the liquid material was steam distilled. Fractionation of the organic distillate gave 242 g. of the desired 1, 3-dibromo-1, 1-difluoropropane.

The autoclave was charged with 2 moles of 1, 3-dibromo-1, 1-difluoropropane, 7 moles of anhydrous hydrogen fluoride and 12 ml. of antimony pentachloride. The autoclave was heated and rocked 18 hours at 150° . The liquid product was steam distilled. Fractionation of the organic distillate gave 157 g. (59%) of 3-bromo-1, 1, 1-trifluoropropane b. 65-70° .

The 3-bromo-1, 1, 1-trifluoropropane, 100 g. (0. 57 mole) was reacted in the customary manner with a solution of 75 g. of potassium hydroxide in 150 ml. of ethanol. The product was collected in a cold trap immersed in Dry Ice and acetone and distilled to give 41 g. of the desired 1, 1, 1-trifluoropropene-2 b. -18 to -16° (11) for a conversion of 74. 5% of the theory.

7. 2-H-Pentafluoropropene

The following series of reactions were followed for the preparation of 2-H-pentafluoropropene used in this research:

$$CF_2Br_2 + CH_2{=}CF_2 \dashrightarrow CF_2BrCH_2CF_2Br$$

$$CF_2BrCH_2CF_2Br + SbF_3 + Cl_2 \dashrightarrow CF_3CH_2CF_2Br$$

$$CF_3CH_2CF_2Br + KOH\ (aq.) \dashrightarrow CF_3CH{=}CF_2$$

The first of the above reactions is reported in detail by Lovelace (17).

A reaction vessel was charged with 137 g. (0.5 mole) of 1,3-dibromo-1,1,3,3-tetrafluoropropane, 75 g. (0.42 mole) of antimony trifluoride and 10 g. (0.14 mole) of chlorine. It was sealed, heated and rocked 12 hours at 50°. The content was steam distilled and the organic distillate was fractionated. There was obtained 26 g. of unreacted $CF_2BrCH_2CF_2Br$, 6.5 g. of $CF_3CH_2CF_3$ b. 0.5-1.0° (13) and 33 g. (31% conversion) of the desired $CF_3CH_2CF_2Br$ with the following constants: b.p. 47.3°, n_D^{20} 1.3228, d_4^{20} 1.784, MR_D calculated for $C_3H_2BrF_5$: 23.82, found: 23.85. Analysis; % bromine calculated for $C_3H_2BrF_5$: 37.5, found: 37.7. When the above reaction was repeated using 137 g. (0.5 mole) of 1,3-dibromo-1,1,3,3-tetrafluoropropane, 75 g. (0.42 mole) of antimony trifluoride and 30 g. (0.42 mole) of chlorine at a temperature of 100° for four hours, only the hexafluoropropane was obtained for a conversion of 85%.

Reaction of 3-bromo-1, 1, 1, 3, 3-tetrafluoropropane, 60 g. (0.28 mole) with a hot solution of potassium hydroxide, 60 g., in 40 ml. of water in the usual manner gave 34 g. of condensed gaseous material. Fractionation of this resulted in 23 g. of the desired 2-H-pentafluoropropene b. -17 to -16° (13) for a conversion of 62%.

An alternate method used to prepare 2-H-pentafluoropropene is indicated by the following reactions:

$$CF_2BrCH_2CF_2Br + KOH\,(aq.) \text{ -------> } CF_2BrCH{=}CF_2 + KBr + H_2O$$

$$CF_2BrCH{=}CF_2 + HF \text{ -------> } CF_3CH{=}CF_2 + HBr$$

The first reaction above is described in detail by Lovelace (17).

The autoclave was charged with 3-bromo-1, 1, 3, 3-tetrafluoropropene-1, 72 g. (0.37 mole) and anhydrous hydrogen fluoride, 15 g. (0.75 mole), heated and rocked five hours at 150°. The gases were vented through a soda lime tower followed by a calcium chloride tower and collected in a trap immersed in Dry Ice and acetone. Fractionation gave 36.5 g. of 2-H-pentafluoropropene for a conversion of 74% of the theory. The infrared spectrum of this material was identical with the spectrum of 2-H-pentafluoropropene prepared by the former method.

8. Perfluoropropene

The perfluoropropene was prepared by pyrolysis of the sodium salt of perfluorobutyric acid (16).

$$C_3F_7COONa \xrightarrow{350°} C_3F_6 + CO_2 + NaF$$

IV SUMMARY

In the course of this research a study has been made of the reaction of 1,2-dibromo-2-chloro- and 1,2-dichloro-2-iodo-1,1,2-trifluoroethane with various fluoroethylenes and fluoropropylenes. The iodine compound gives excellent yields of addition products even with olefins which fail to react with the dibromide. The high yields of adducts from these perhaloethanes and the ease with which the addition compounds can be dehydrohalogenated and dehalogenated affords a good synthetic method for the preparation of various fluoroölefins and fluorobutadienes which contain the perfluorovinyl group. In this manner twelve new addition products have been prepared which were converted into nine new fluoroölefins and six new fluorobutadienes.

In addition a convenient laboratory synthesis of 2-fluorobutadiene-1,3 from butene-2 has been described. This method uses commercially available materials and can be carried out with laboratory apparatus, thereby avoiding the use of special equipment and handling of the highly explosive material required in the catalytic addition of anhydrous hydrogen fluoride to vinyl acetylene.

A study of the infrared absorption spectra of fluorine-containing olefins and dienes has been made and a pronounced shifting of the carbon-carbon double bond stretching vibration in the direction of shorter wavelengths was observed. Absorption frequencies for the carbon-carbon double bond stretch have been assigned for the groups, CHR=CR-, where R represents a hydrogen atom, a methyl group, or a trifluoromethyl group, CHF=CH-, CF_2=CH- and CF_2=CF-.

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ACKNOWLEDGEMENTS

The author wishes to take this opportunity to express his appreciation to those whose assistance, advice and encouragement have contributed greatly to the success of this research.

To Dr. Paul Tarrant, director of this research and Chairman of the Supervisory Committee, whose creative ideas, inspiration and willing assistance have been essential factors in the success of this work, grateful thanks is extended.

To the members of the Supervisory Committee, whose aid and cooperation during the course of this study is greatly appreciated.

To Miss Mary Louise Van Natta for the valuable infrared spectra used in this research the author extends his appreciation.

The assistance and many helpful suggestions given by the author's fellow students and coworkers, Dr. A. M. Lovelace, Messrs. R. E. Taylor, B. E. Gray and F. F. Norris are gratefully acknowledged.

The success of this research is due in no small part to the patience, encouragement and cooperation shown by the author's wife. To her no written acknowledgement is adequate.

The author wishes also to express his appreciation to Dr. J. C. Montermoso of the office of the Quartermaster General for the financial support which has made this research possible.

BIOGRAPHICAL NOTES

Marvin Russell Lilyquist was born October 2, 1925 in Barnum, Minnesota. He moved to Sebring, Florida at an early age and attended the public schools of that city.

He began his college studies at Manchester College, North Manchester, Indiana in September, 1944 and received the degree Bachelor of Arts from that school in June, 1948. While an undergraduate he served as a student assistant in the Department of Chemistry.

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This dissertation was prepared under the direction of the Chairman of the candidate's Supervisory Committee and has been approved by all members of the Committee. It was submitted to the Dean of the College of Arts and Sciences and to the Graduate Council and was approved in partial fulfilment of the requirements for the degree Doctor of Philosophy.

January 29, 1955

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